Structure and Properties of Magnesia for Use in Pebble Bed Heaters To 4000°F

J. O. No. 369 February 1, 1963

Prepared for

NASA AMES RESEARCH CENTER
Moffett Field, California

under
Contract No. NAS 2-1152

ADVANCED MATERIALS AND PROCESSES
923 N. San Antonio Road
Los Altos, California

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I. INTRODUCTION

The over-all objective of this investigation is to develop magnesia refractory pebbles of suitable properties for use at temperatures up to 4000°F in the pebble bed air heater for the 3.5 ft. wind tunnel facility at ARC. A systematic study was undertaken to achieve the necessary combination of thermal shock resistance and compressive strength to meet operational requirements. The most promising structural conditions are specified, and optimum process conditions are defined on the basis of current results.

Fifty pebbles of approximately 7/8-inch diameter were produced by techniques developed during the investigation and submitted to Ames for evaluation.

II. CURRENT APPROACH

Refractory pebbles for use at 4000°F must not deform, spall, or stick together under operating conditions which involve severe thermal shock and compressive loading. To meet this application, magnesia pebbles must possess a suitable combination of high chemical purity, thermal shock resistance, and compressive strength under point loading. In addition, the practicality of producing large quantities of pebbles to appropriate specifications must not be overlooked. Therefore, the following considerations were established to provide a framework within which detailed data was produced and analyzed:

1. MgO of maximum available purity must be employed to achieve the highest possible melting point and to minimize the volume of low-melting oxide and silicate phases. In particular, the presence of a continuous, glassy grain boundary constituent cannot be tolerated.

This requirement for maximum purity, coupled with practical considerations, defines the use of 98+% pure MgO, which is readily available from commercial sources.

2. A refractory body of controlled porosity (pore size and distribution) and suitable particle size distribution can exhibit superior thermal shock resistance, as compared to bodies of nearly theoretical density. Thus, MgO pebbles of much less than theoretical density should be applicable to the current problem, if adequate mechanical strength can be maintained.

3. To evaluate the effect of structure, as-pressed ("green") compacts can be produced covering a range of densities as determined by particle size composition. Subsequently, "green" compacts can be fired at sufficiently high temperatures and times to insure structural stability under the ultimate service conditions and to provide adequate mechanical strength (bonding).

4. Thermal and mechanical properties must be correlated with structures to produce refractory pebbles possessing the optimum combination of properties for the application.

III. EXPERIMENTAL PROCEDURES

1. Raw Materials

MgO powder was obtained from a number of commercial suppliers, including Norton and Kaiser, to examine the effects of impurities on high temperature behavior. Experience has shown that MgO of 98% purity has high strength at elevated temperatures and is economically feasible as a material to be used in large quantities. Powder lots obtained from several sources are compared in Table I.

Initially, powder was spheroidized by firing through a plasma-arc gun. Compacts produced from this "ideal" powder were compared with those made of as-received powder. Since the as-received powder particle shape is roughly spherical, no advantage was observed in going to the plasma-spheroidized particles; therefore, this preliminary step was abandoned.

2. Production of Green Compacts

For initial studies, a simple 1-inch diameter by 1-inch cylindrical specimen was employed. MgO powder from various sources was separated into size fractions and a number of single, binary, and ternary mixtures was produced. During this

portion of the program, analytical methods were used to predict mechanically-packed densities by assuming closely-packed spheres of various particle size compositions. Cold pressing was carried out on dry compacts at about 17, 500 psi on a hydraulic press.

3. Sintering

A number of compacts was pre-sintered at 1500°C (2750°F) for 8 hours to produce a body which could be more easily handled. This pre-sintering had no effect on subsequent high-temperature firings, and was discontinued in the latter phases of the program.

High-temperature sintering (4000°F) was conducted in a graphite furnace under a helium atmosphere.

4. Structure and Properties

Thermal shock tests were performed at 4000°F in a carbon-resistance furnace by cooling the specimens at controlled rates, using helium cooling gas. Rates varied from 50 to over 250°F / min. from 4000°F.

Compression tests were conducted on compacts at room temperature by compressing between two 1/2-inch diameter steel balls. This method of testing produced relative strength values which were useful for screening purposes.

Structural characteristics of all specimens were examined using conventional metallographic methods. Observations were then correlated with test results and density measurements. Mechanical polishing of specimens was conducted using alumina abrasive for final polishing. As-polished specimens were examined microscopically for phases present, porosity distribution, and particle size; while etched sections were employed for grain size measurements and phase identification. The etch consisted of cold 50% HNO_3 - H_2O.

Density measurements were conducted in accordance with standard procedures set forth in ASTM, C20-46.

Production of spherical pebbles involved selected binary mixtures which were cold-pressed at approximately 20, 000 psi in a five-piece mold set, consisting of a containing cylinder and two-piece, concentric, end plungers. The double end plunger unit was used to facilitate removal of the 7/8-inch diameter MgO pebbles

without parting, due to sticking of the MgO to plunger surfaces. Pebbles were sintered at 4000°F for one hour in the graphite-resistance, helium atmosphere furnace.

IV. EXPERIMENTAL RESULTS

Single, binary, and ternary mixtures were prepared and sintered as discussed previously. Table II lists a number of the mixtures which were examined during this program. Table III includes results of various sintering treatments on density.

1. Single Particle Size Compacts

Powders of various purities were compacted in the particle sizes shown in Table IIA. Green compacts of single size components exhibited approximately 60% of theoretical density. The ideal value for close packing of spheres is 60.5% for orthorhombic packing. The microstructure of impure powder is exhibited in Figure 4-1. This 93% pure powder was sintered at 3300°F and had a density of 91% theoretical. Very little porosity is in evidence; however, an intergranular network of SiO_2 and CaO can be seen, together with considerable amounts of metallic impurities (the white areas). This structure is typical of pebbles submitted by commercial sources during early phases of the ARC pebble bed heater program. The continuous, glassy, intergranular network forms a liquid at temperatures as low as 3000°F and, thus, would deprive the compact of the high temperature strength necessary for the current application. No subsequent work was performed on low purity raw materials.

The three other powders (Kaiser, Norton, Special Grade) exhibit impurities comparable to their 98+% MgO analysis (Figure 2). The low impurity level prevents a continuous intergranular network from forming and is satisfactory for current purposes.

A summary of sintering experiments performed on single particle size bodies is compiled in Table IIIA. The rate of density increase is chiefly a function of particle size at the temperatures employed. The drop in density of sample A9 after sintering at 4000°F, as compared to the lower temperature treatments, may be explained by growth of large bubbles due to gas migration to these regions. Furthermore, grain growth associated with the 4000°F treatment indicates that heat treatments carried out at lower temperatures do not produce sufficient structural stability for the ultimate application. Consequently, all further work was performed at 4000°F.

2. Binary Compacts

Various binary systems were studied to determine as-compacted density as a function of powder size composition. Typical results are shown graphically in Figure 1 and are tabulated in Table IIB.

The results of heat treatment on binaries are compiled in Table IIIB. Initial sintering was performed on two maximum density compacts: 62 1/2% - 177μ + 37 1/2% - 37μ (B4) and 55% - 149μ + 45% - 2μ (B10). To achieve final densities exceeding 76% of theoretical, compacts were made using greater percentages of the fine 2μ powder. These compacts behaved as if density was governed entirely by the sintering rate of the larger particles for compacts consisting of only 30% of the larger particle; the sintering rate of the finer particle appeared to become more important as its percentage reached 90% of the total. Further work is necessary to fully predict this behavior.

In general, the binaries studied gave evidence of being porous, but tightly bonded bodies which would maintain structural stability at 4000°F. However, the 30-70% (B19) and 10-90% (B18) compacts tended to sinter rapidly in regions comprised entirely of 2μ particles and to separate at boundaries between such regions in the compact. This undesirable situation is exhibited in Figure 3-2 for compact number B19. By comparison, photomicrographs 1, 3, and 4 are shown in Figure 3 to indicate the desired porosity distribution, as exhibited by the most promising compositions examined. Porosity in single-particle-size compacts involves larger, more evenly distributed pores (Figure 2). The large particles necessary for high temperature stability involve a structure in which small inhomogeneities no longer remain negligible. The binary compacts, though possessing some regions of lower porosity than the single-particle-size compacts, have large interconnecting regions of high porosity which appear to improve high temperature behavior.

3. Ternary Compacts

Although binaries and single particle compacts approximated densities expected on the basis of packing of ideal spheres, ternary compositions did not produce suitable results. This is explained on the basis of available particle size ratios which were not large enough to give the desired packing densities. Typical ternary compositions studied are given in Table IIC. Sintered compacts produced inhomogeneous microstructures which contained regions of separation, as discussed previously. Such results offered to improvement over binary compositions and, therefore, little additional effort was expended in this direction.

4. Properties

Thermal shock resistance represents one of the most important requirements for acceptable MgO pebbles. Most of the binaries survived all thermal shock tests; whereas, the high density single-particle-size compacts cracked. Typical results of these tests are summarized in Table IV. No grain growth nor density change was noted in any of the tests. The bar chart indicates cooling rates at or below which no cracking occurred (test samples were multi-cycled at successively higher cooling rates).

Results of point loading compression tests are shown in Table V. Although variations in penetration strength were observed to be relatively minor, it can be concluded that density was not very important within the range studied. 93% dense compacts proved weaker than the 80% dense compacts. Particle size and pore distribution were relatively more important factors. For example, the strength of the high density (B18) binary was not superior to other binaries because of structural inhomogeneities. These results permitted selection of two binary compositions of maximum interest for further evaluation, namely B4a and B16. The low density (70%) of B4a maintained compressive strength within the range of measured values while providing outstanding thermal shock resistance. Binary B16, on the other hand, combines exceptionally high strength with reasonably good thermal shock resistance. Both analyses possess very homogeneous microstructures.

5. Pebbles from Other Sources

MgO pebbles received by ARC from other sources were examined during the current study to a minor extent. As shown in Figure 4-3 and Figure 4-4, gross inhomogeneity characterizes the structure of pebbles produced by two different suppliers. The Norton pebbles contain an extremely wide particle size range, resulting in regions of separation, as well as numerous large, unbonded, particles. The Harbison-Walker product contains a wide range of particle sizes, which produces a completely random, inhomogeneous, distribution of pores and particles. Both pebble types are relatively low in density, but exhibit acceptable penetration strength (see Table VII). The Minneapolis-Honeywell product is very dense, but does not appear to offer a strength advantage over other pebbles tested. In addition, for a given size, the high density pebbles are considerably less thermal shock resistant than lower density types of adequate mechanical strength and purity.

V. SUMMARY AND CONCLUSIONS

Controlled particle size composition, coupled with adequate purity, appear to offer much promise in connection with the pebble bed heater application. High densities in single-size compacts provided high strength, but low thermal shock resistance. Binary compositions proved capable of high thermal shock resistance and, at the same time, maintained high compressive strength.

From this modest investigation, the following compositions appear to offer the most promise for the application under consideration: no. B4a (62 1/2% - (177-149)μ + 37 1/2% - 37μ) MgO powder (70% density after sintering), and no. B16 (50% - (62-44)μ + 50% - 2μ) MgO (79% density after sintering). For future reference, the former has been designated as Type I pebbles (< 75% density) and the latter has been designated Type II pebbles (> 75% density). Two choices appear to be appropriate at this stage of development for comparison during subsequent evaluations conducted at Ames. Additional work, outlined in the following section, is indicated to define truly optimum pebble processing conditions for the ultimate application. For structural stability of MgO pebbles, the selected compositions must be processed at 4000°F. For periods studied, 0-4 hours, no change in density was noted for compacts having a sizable percentage of particles greater than 100μ in diameter. Grain growth after sintering has not appeared to be severe for these periods. Whether such compacts will retain their present density and porosity distribution, or whether, in time, they will become denser with a very large grain size is not known, but is not expected.

Fifty pebbles were produced for evaluation by Ames. Of these, thirty were of the lower density, Type I, and twenty of the higher density, Type II. Table VI gives complete data on each lot of pebbles submitted to ARC for evaluation. For comparison, Table VII and Figure 4 present information on pebbles received from other sources. It can be concluded that the pebbles produced as a result of this investigation combine the best qualities of each with regard to thermal shock resistance, room temperature penetration strength, and structural homogeneity. Thus, on the basis of available data, pebbles Type I and/or Type II should closely approximate the optimum solution to this difficult problem.

VI. RECOMMENDATIONS FOR FUTURE WORK

Results appear to warrant additional work aimed at optimizing both structural and processing factors. On the basis of completed work, it has been concluded that compacts can be produced with adequate strength and thermal shock resistance, if material of suitable purity, particle size, and porosity distribution is produced. A number of single component, binary and a few ternary particle size compositions have been evaluated. Because of the many possibilities remaining, it appears that additional work should be conducted on the investigation of binary, ternary, and more complicated systems for comparison with current results.

Quantitative tests were not employed in the current study because of limitations already mentioned. However, such tests should be conducted on the most promising compositions already developed, as well as on new compositions offering some potential for high temperature applications. In particular, a quantitative thermal shock test should be employed together with conventional compression tests, and these correlated with structure to a greater extent than has been done on past work.

Structural stability (pore size, grain size) should be studied as a function of time at 4000°F for much longer times than has been done to date. Finally, since large quantities of pebbles are involved, a practical production process should be developed and evaluated from the economic standpoint.

As the next step in the development of MgO pebbles for the 4000°F heater application, the following program is proposed:

1. Additional research and development along the lines discussed above, to provide needed information for production of pebbles representative of optimum structural and processing conditions.

2. Production of a pilot plant quantity (800 lbs.) of pebbles produced by the optimum process.

TABLE I

Chemical Analysis of MgO Powder from Several Sources

	Source			
Impurity	Kaiser	Norton	Special Grade (2μ) *	Kaiser
MgO	98+ %	98+ %	98+ %	93+ %
SiO_2	0.46	0.77	0.67	5.4
CaO	.7	.8	.16	.95
Fe_2O_3	.3	---	.24	.34
Cr_2O_3	.11	---	---	---
Al_2O_3	.1	---	---	---
B_2O_3	.2	---	---	---

* Special grade denotes a fine, 2μ (micron), high purity U. S. P. grade of MgO.

TABLE II

Summary of Particle Size Compositions Investigated

A. Single Component Mixtures

No.	Powder Source	Particle Size		"Green" Density * (% of theoretical)
		μ(Microns)	Mesh Size	
1	Kaiser - 98+% purity	+177	+ 80	60
2	" "	149-177	- 80 +100	60
3	" "	149-74	-100 +200	60
4	" "	74-62	-200 +250	60
5	" "	62-44	-250 +325	60
6	" "	44-37	-325 +400	60
7	" "	-37	-400	61
8	Norton - 98+% purity	-44	-325	61
9	Special Grade - 98+% purity	2	---	57
	Ideal Spheres (orthorhombic packing)			60.5

* Density determined after blending and cold compacting powder mixture at R. T. under 17,500 psi pressure. No binder was used.

TABLE II (cont.)

B. Binary Mixtures

No.	Powder Type	Particle Sizes				"Green" Density
		Component 1		Component 2		
		%	Size (μ)	%	Size (μ)	
1	Kaiser, 98+%	25	177	75	37	65
2	" "	40	177	60	37	68
3	" "	50	177	50	37	71
4	" "	62.5	177	37.5	37	73
4a	" "	"	177-149	"	"	67
5	" "	70	177	30	37	71
6	" "	90	177	10	37	65
7	" "	45	149	55	37	68
8	" "	60	149-74	40	37	68
9	" "	50	149-74	--	--	--
	Special Grade, 98+%	--	--	50	2	69
10	Kaiser, 98+%	55	149-74	--	--	--
	Special Grade, 98+%	--	--	45	2	70
11	Kaiser, 98+%	60	149-74	--	--	--
	Special Grade, 98+%	--	--	40	2	69
12	Kaiser, 98+%	65	149-74	--	--	--
	Special Grade, 98%	--	--	35	2	68
13	Kaiser, 98+%	70	149-74	--	--	--
	Special Grade, 98%	--	--	30	2	67
14	Kaiser, 98+%	80	149-74	--	--	--
	Norton, 98+%	--	--	20	2	66
15	Kaiser, 98+%	30	62-44	--	--	--
	Special Grade, 98+%	--	--	70	2	65.5
16	Kaiser, 98+%	50	62-44	--	--	--
	Special Grade, 98+%	--	--	50	2	66.5
17	Kaiser, 98+%	70	62-44	--	--	--
	Special Grade, 98+%	--	--	30	2	64
18	Kaiser	10	149-177	--	--	--
	Special Grade	--	--	90	2	63
19	Kaiser	30	149-177	--	--	--
	Special Grade	--	--	70	2	65

TABLE II (cont.)

C. Ternary Mixtures

No.	Powder Type	Particle Sizes						"Green" Density
		Component 1		Component 2		Component 3		
		%	Size (μ)	%	Size (μ)	%	Size (μ)	
1	Kaiser - 98+%	50	177	16 2/3	74-62	33 1/3	37	70.1
2	" "	43	177	28	74-62	28	37	69.5
3	" "	37 1/2	177	37 1/2	74-62	25	37	68.8
4	" "	60	177	30	74-62	10	37	68.3
5	" "	60	177	20	74-62	20	37	69.3
6	" "	70	177	20	74-62	10	37	68.3
7	" "	70	177	10	74-62	20	37	70.4
8	" "	40	149-177	10	44-37	--	--	--
	Special Grade, 98+%	--	--	--	--	50	2	69
9	Kaiser - 98+%	20	149-177	20	44-37	--	--	--
	Special Grade, 98%	--	--	--	--	60	2	65.5

TABLE III

Effect of Sintering Conditions on MgO Pressed Compacts

A. Single Particle Size Compacts

Temperature:		R. T.	3300°F	3300°F	3800°F	4000°F	4000°F	4500°F
Time:			4 hrs.	8 hrs.	4 hrs.	2 hrs.	1 hr.	1 hr.
Compact No. *								
A4:	Density	60%	66	66	66	67	--	--
	**G. S.	25	--	--	--	--	--	--
A7:	Density	61%	75	77	79. 5	80	80	81. 5
	G. S.	25	25	35	50	45	60	48
A8:	Density	61%	72. 5	74	77. 5	76	75	78
	G. S.	30	30	37	--	--	56	--
A9:	Density	57%	93	93	92. 5	90. 5	92	93
	G. S.	45	45	62	87	62	75	75

* Numbers refer to TABLE II.

** Grain size - average diameter in microns.

TABLE III (cont.)

B. Binary Compacts

Temperature, °F:		R. T.	3300	3300	3800	4000	4000
Time, hrs.:		--	4	8	4	1	2
Compact No.							
B4:	Density	73	75	75	76	76	76.5
	G. S.	15, 70	15, 70	20, 80	37, 90	50, 100	--
B4a:	Density	67	--	--	--	70	--
	G. S.	15, 70	--	--	--	40, 90	--
B10:	Density	70	--	--	--	76	--
	G. S.	2, 70	--	--	--	30, 85	--
B15:	Density	65.5	--	--	--	78	--
	G. S.	2, 70	--	--	--	30, 90	--
B16:	Density	66.5	--	--	--	79	--
	G. S.	2, 70	--	--	--	30, 90	--
B17:	Density	64	--	--	--	73.5	--
	G. S.	2, 70	--	--	--	30, 90	--
B18:	Density	63	--	--	--	89.5	--
	G. S.	2, 70	--	--	--	40, 90	--
B19:	Density	65	--	--	--	78	--
	G. S.	2, 70	--	--	--	40, 90	--
C. Ternary Compacts							
C8:	Density	69	--	--	--	77	--
	G. S.	--	--	--	--	--	--
C9:	Density	65.5	--	--	--	75	--
	G. S.	--	--	--	--	--	--

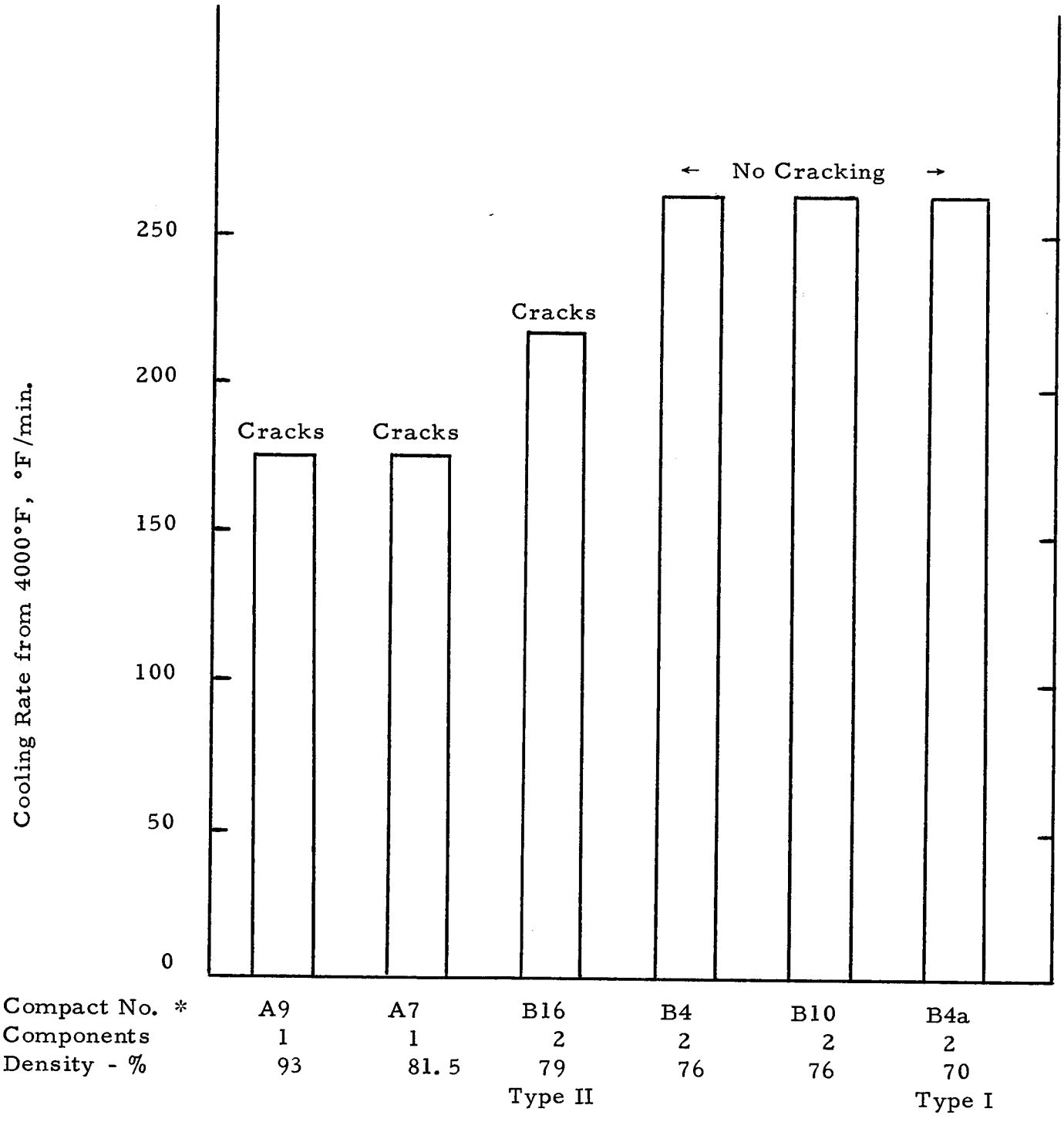


TABLE IV

Thermal Shock Behavior of Typical MgO Compacts

* Numbers refer to TABLE II.

TABLE V

Room Temperature Rupture Strength of MgO Compacts

No.	Density, %	Rupture Load, lbs.	Comments
A9	93	1275	Compacts - poor thermal shock resistance
A7	81.5	1530	Compacts - poor thermal shock resistance
B4	76	1200	Compacts - good TSR
B10	76	775	Compacts - good TSR
B15	78	765	Compacts - good TSR
B16	79	1275	Compacts - fair TSR
B18	89.5	1190	Compacts - poor TSR
C8	77	935	Compacts - good TSR
C9	75	1020	Compacts - good TSR
B4a	70	850	Type I pebbles - good TSR
B16	79	1700	Type II pebbles - fair TSR

Note: Maximum load (lbs.) to fracture in compression between 1/2" diameter steel balls (average values).

Compact numbers refer to TABLE II.

All compacts and pebbles were sintered at 4000°F for 1 hour.

TABLE VI

MgO Pebbles Submitted to Ames for Evaluation

Type	I	II
No. Submitted	30	20
Composition	62 1/2% 177 - 149μ 37 1/2% 37μ	50% 62-44μ 50% 2μ
Sintering Treatment	4000°F - 1 hr.	4000°F - 1 hr.
Density	70%	79%
R. T. Penetration	850	1700
Thermal Shock Resistance	Excellent (>250°F/min.)	Fair-Good (>200°F/min.)
Microstructure	See Fig. 3	See Fig. 3
Chemical Analysis:		
MgO	98. + %	98. + %
SiO_2	0. 44	0. 47
Fe_2O_3	0. 21	0. 21
Cr_2O_3	0. 1	0. 1
CaO		

TABLE VII

Pebbles from Other Sources

	Size (dia.)	Density (% theo.)	R. T. Penetration (lbs.)
Minneapolis-Honeywell *	1/2 in.	98	765
	1	98	1360
Harbison-Walker - Lot 29	1 1/4	73	2100
	1	--	1200
Harbison-Walker - Lot 30	1 1/4	77	2100
	1	--	1200
Harbison-Walker *	1	73	1530
Norton *	7/8	79	1275
Kaiser	7/8	93	930
Ampro Type I	7/8	70	950
Ampro Type II	7/8	79	1700
Remy Al_2O_3	1 1/8	--	3300

* Specimens obtained from ARC. See Fig. 4 for microstructures.

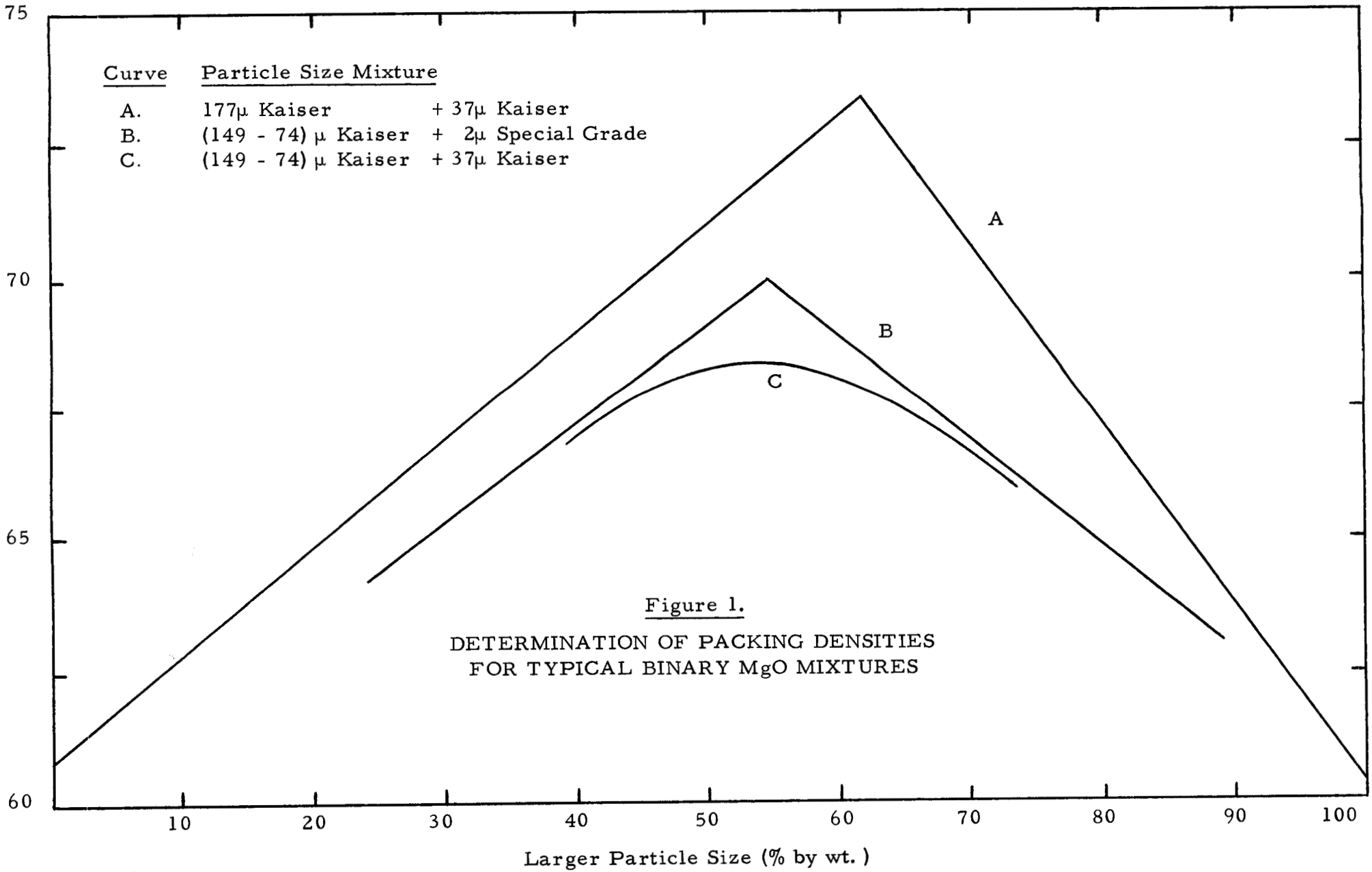
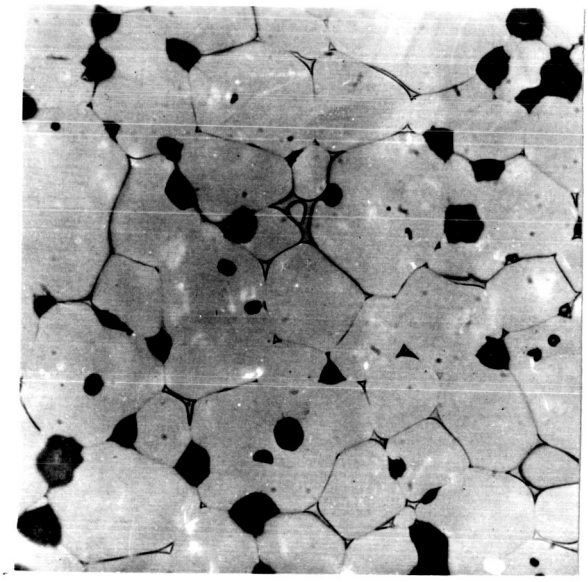


Figure 1.

DETERMINATION OF PACKING DENSITIES
FOR TYPICAL BINARY MgO MIXTURES

FIGURE 2.



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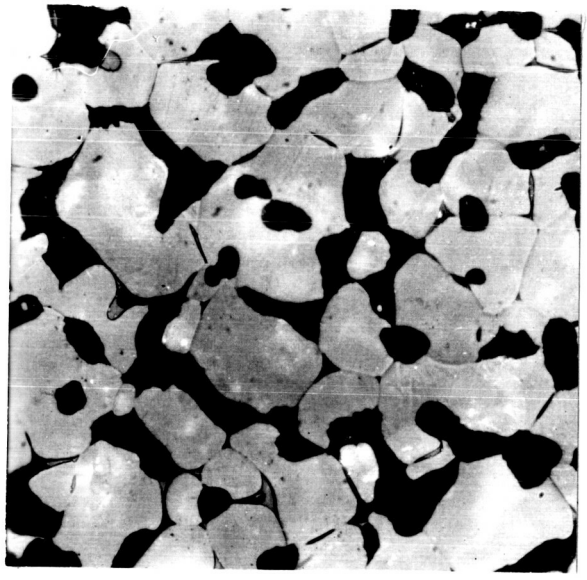

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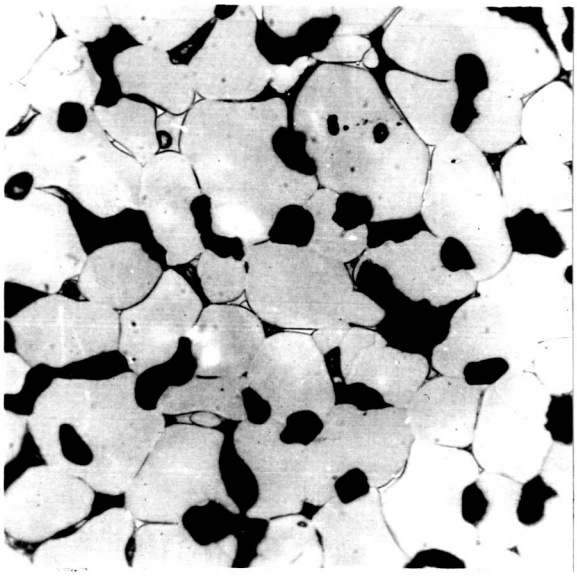

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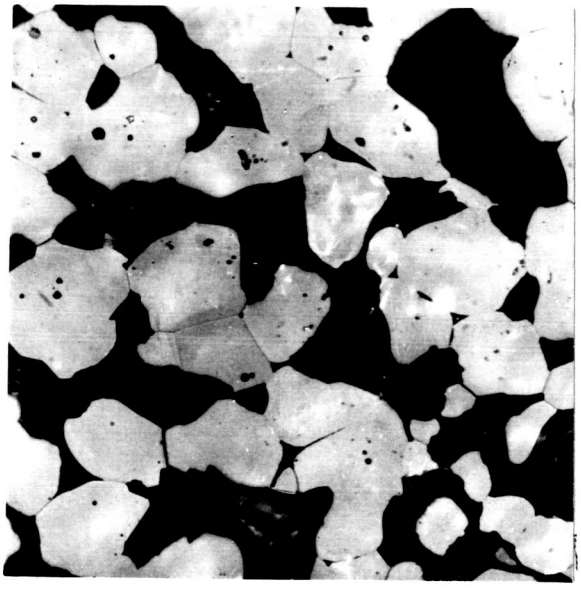

4.

Typical Single Particle Size Sintered Compacts

1.	Special Grade (2μ)	:	4000°F, 1 hour	Density - 92%
2.	Norton (-44μ)	:	4000°F, 1 hour	Density - 75%
3.	Kaiser (-37μ)	:	4000°F, 1 hour	Density - 80%
4.	Kaiser (74-62μ)	:	4000°F, 1 hour	Density - 67%

All photomicrographs: 200X, Unetched

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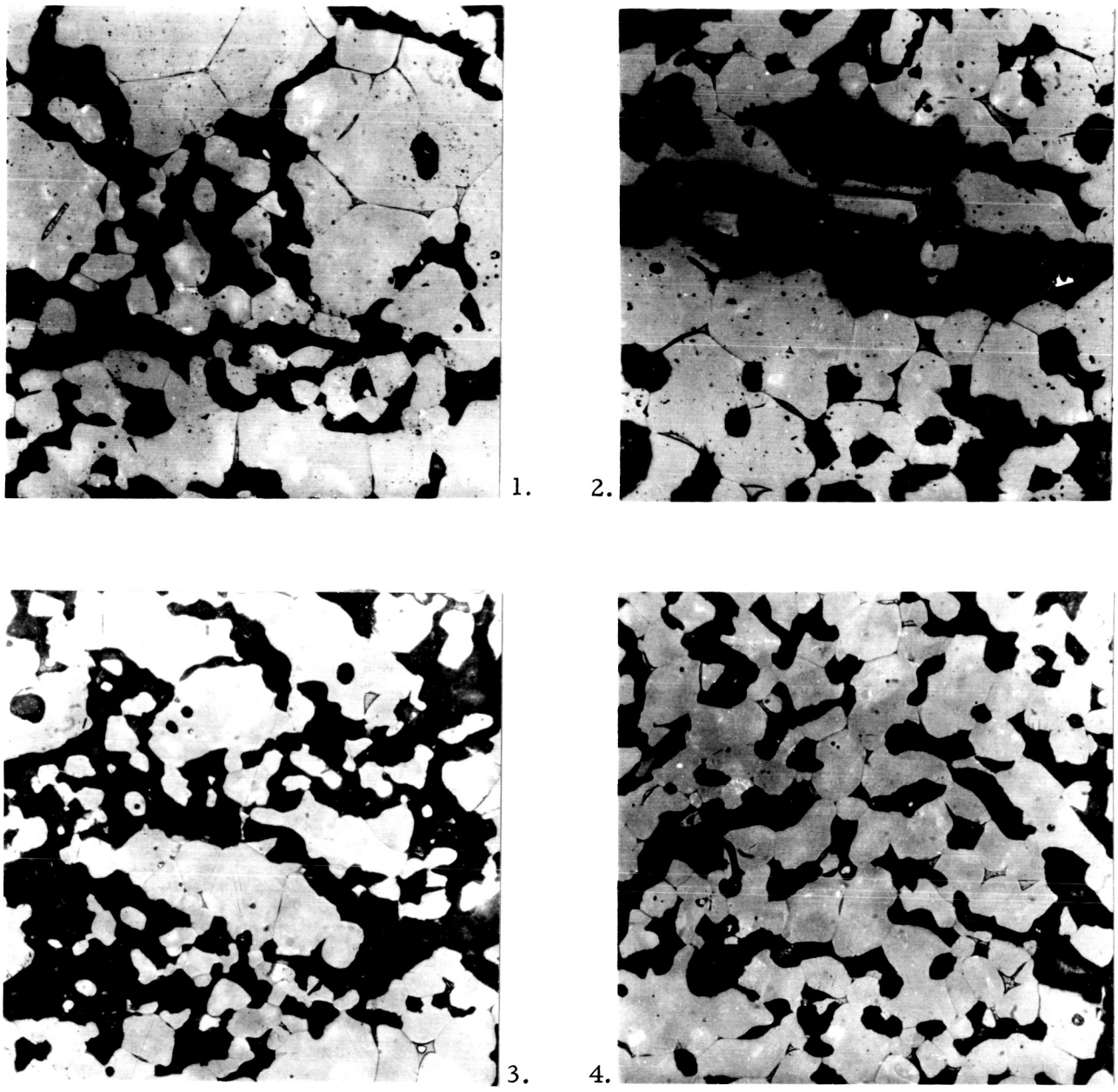
FIGURE 3.



1. 2. 3. 4.

Typical Binary Sintered Compacts

1.	B4	4000°F, 1 hour	Density - 76%
2.	B19	4000°F, 1 hour	Density - 78%
3.	B4a (submitted to ARC)	4000°F, 1 hour	Density - 70%
4.	B16 (submitted to ARC)	4000°F, 1 hour	Density - 79%

All photomicrographs: 200X, Unetched

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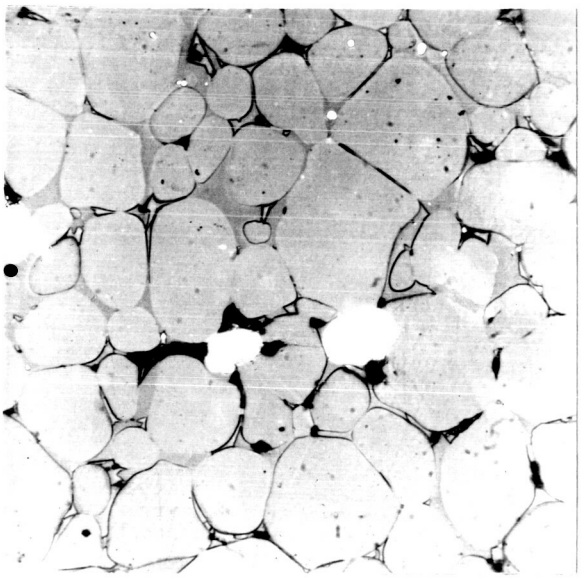
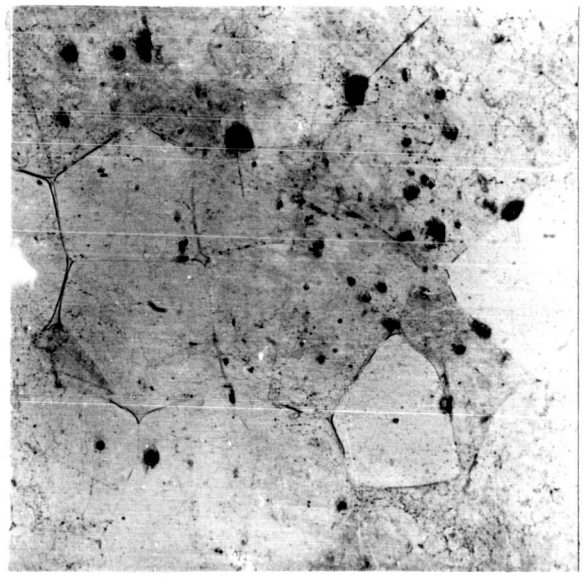
FIGURE 4.



1.



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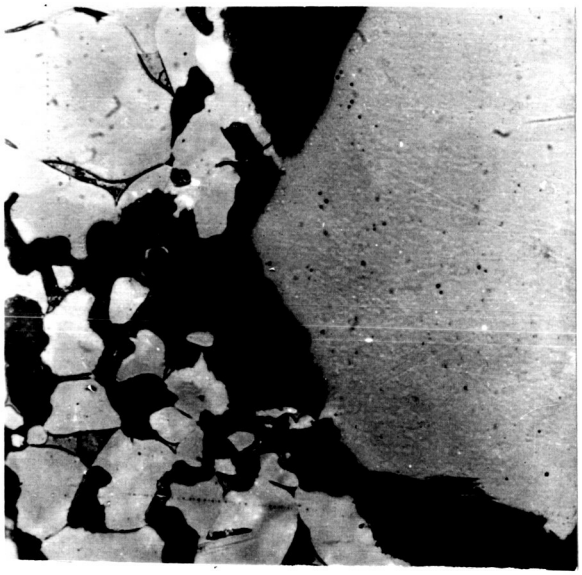

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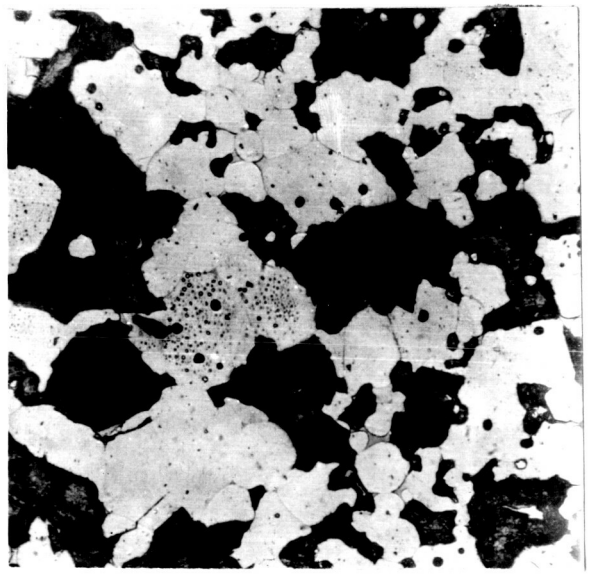

4.

Compacts from Other Sources

1.	Kaiser 93+% purity	3300°F, 4 hr.	Density - 91%
2.	Minneapolis-Honeywell (submitted to ARC)	4000°F, 1 hr.	Density - 98%
3.	Norton MgO (submitted to ARC)		Density - 79%
4.	Harbison-Walker (submitted to ARC)		Density - 73%

All photomicrographs: 200X, Unetched

ADVANCED MATERIALS AND PROCESSES
923 N. San Antonio Road
Los Altos, California