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EVALUATION OF BINDERS FOR
MACHINABLE UNFIRED CERAMICS

by

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ABSTRACT

Twenty-seven different combinations of binders were mixed with alumina powder to study tensile strength in unfired oxide parts and its relationship to machinability. Isostatically pressed oxides were impregnated with waxes to further increase their mechanical strengths for machining. Alumina, magnesia, zirconia, and zircon bars containing 4.0 percent polyvinyl alcohol were tested to compare the strength of equal amounts of binder in different oxides. In these bars the variation in tensile strengths was found to be due mainly to difference in particle size. Machinability was found to improve as the binder tensile strength increased.

INTRODUCTION

The object of this study was to find the most suitable temporary binders for strengthening powder compacts of oxide ceramics. The binders must provide sufficient strength so that the compacts can be handled and machined. Precision parts machined from these compacts will subsequently be fired to obtain maximum density and strength. It is required that the binders are completely expelled during firing. The alternate to fabricating precision parts from unfired ceramics is to diamond grind them after they are fired. Parts with reasonable tolerances can be machined from unfired compacts; if close tolerances are required, diamond grinding is necessary.

Machined parts usually require a smooth finish. To obtain a good finish, experience has indicated that the material used for the machinable ingot must be a fine powder with the binder uniformly dispensed throughout the material.

Levine⁽¹⁾, Wild⁽²⁾, Thompson⁽³⁾, Gormly⁽⁴⁾, and Whittemore⁽⁵⁾ list and discuss binders for fabricating ceramics by the extrusion method. Threischel and Emrich⁽⁶⁾, McNamara and Comeforo⁽⁷⁾ tested the strength of binders in extruded clays by modulus of rupture. No references were found pertaining to binders for machinable oxide compacts.

EXPERIMENTAL PROCEDURE

Aluminum oxide* powder was used for most of the tests in this study because of its relatively low cost. The binders were selected on the basis of whether they could be mixed with water and added to aqueous oxide suspensions. Table I lists the binders and impregnating waxes that were evaluated in this study. Most of the binders were made into solutions before use to assure complete dispersion during processing. Four different oxides were mixed with

the same binder to compare the strength of one binder in different oxides.

The powders for the test samples were prepared by spray drying. All the oxides were ball milled for 4 hours prior to spray drying. The oxide suspensions and binder solutions were mixed after milling. The spray dried powders had an average particle size of 15 microns. Spray-dried powders are uniformly coated by the binders and are spherical; thus, they are free flowing.

The test ingots (3/4 in. by 3/4 in. by 6 in.) were formed by isostatic pressing at 20,000 psi. The powders were vibrated into rubber molds and pressed in a hydrostatic pressure vessel. Isostatic pressing was used because it gives the most uniform compact from the standpoint of shrinkage and density.

A series of test bars containing 3.5 percent Methocel® were impregnated with waxes to determine if this would further increase the unfired tensile strengths. This was accomplished by first preheating the waxes and the test bars to 250°F and then immersing the bars in the wax. The time required for the waxes to impregnate a 3/4-inch square cross section is given in Table II.

A study was made to determine if there is a relationship between machinability and the tensile strength of the ingots. Test parts (Figure 1) were machined and tensile strength tests made on the same batch of samples. The test parts were machined on a lathe at 1000 rpm using a feed of 0.0025 in. per revolution and a 0.025-in. depth of cut with a tungsten carbide tool. The tensile strengths of the samples were measured on a Instron testing machine using a cross-head speed of 0.02 in. per minute. The bars were gripped by padded C-clamps for the tensile tests.

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Figure 1. TEST PART TO RELATE MACHINABILITY OF UNFIRED OXIDE CERAMICS TO THE TENSILE STRENGTHS OF BINDERS

* Alcoa Type A-14, 325 mesh.

® Methocel (methylcellulose) Trademark The Dow Chemical Company.

RESULTS

Data for the tensile strength of bars impregnated with waxes are shown in Table II. The polyethylene glycol and the Carnauba wax gave the highest tensile strengths for the waxes tested (643 and 649 psi), however, the polyethylene glycol did not completely impregnate the bars.

The tensile strengths of the test bars containing various binders are given in Table III. Polyvinyl alcohol and mixtures of polyvinyl alcohol with glycerol or polyethylene glycol give the highest tensile strengths for the binders tested (123-132 psi). The same amount of polyvinyl alcohol mixed with a wax emulsion gave a binder tensile strength of only 70.9 psi.

Five compositions containing 4.0 percent polyvinyl alcohol were also tested for tensile strength (Table IV). The 85 percent alumina body was a chemical porcelain mixture. This mixture gave the highest tensile strength (296.8 psi) for the alumina compositions.

Machinability of the unfired test part was compared to binder tensile strengths that ranged from 60-650 psi (Table V). Binders having tensile strengths of less than 60 psi did not have sufficient strength for machining this part.

DISCUSSION OF RESULTS

Polyvinyl alcohol gave the highest tensile strength results in the binder study. Polyvinyl alcohol used with -325 mesh starting material will consistently give tensile strengths of approximately 200 psi.

When using the same amount of binder, there appears to be little change in binder strength among different oxides. Data in Table IV indicates that the starting grain size is the greatest factor in strength variation. All the oxides listed in Table IV were milled for four hours.

The -200 mesh magnesia and zirconia gave approximately the same tensile strength results (Table IV). This indicates that there is no effect from hydroxide bonding that

is usually present in cast magnesia ware. There probably would have been bonding present if the magnesia suspensions had been allowed to age before spray drying. The high tensile strength from the 85 percent alumina composition was probably due to the presence of clay bonding.

Waxes can be used as impregnating agents to increase tensile strengths up to 650 psi. Polyethylene glycol and bees wax would not be practical to use because they require too long a time to saturate the ingots. The test parts machined from ingots containing binders having tensile strengths of less than 140 psi had a very rough surface finish. Parts machined from ingots which were impregnated with waxes had sharp edges and a very smooth finish.

The lower 95 percent confidence limit would be very low in most of the tensile strength tests.* This range in tensile strength was caused by the C-clamp holders being slightly out of alignment on the specimens. It is believed that the data could have been greatly improved by using standard tensile specimens and a holding chuck. However, it was impossible to machine standard tensile strength specimens from the weaker samples.

SUMMARY

Using standard machine tools, unfired oxide compacts can be bored, broached, threaded, turned and milled.

Machinability was found to be related to binder tensile strength in the following way: Tensile strengths of 150-300 psi are necessary for fabricating short parts with a smooth finish and strengths of 300-600 psi are required for machining longer parts with a very smooth finish.

* Statistics - Ninety-five percent of the data should fall between the $\bar{Y} \pm 3S$ limits if the data is from a normal distribution.

$$S^2 = \frac{N\epsilon\bar{Y}^2 - (\epsilon Y)^2}{N(N-1)}$$

Where: S = standard deviation
N = number of tests
 ϵ = summation of values
Y = actual test values
 $\bar{Y}$ = average Y

APPENDIX

TABLES

TABLE I

BINDERS AND WAXES THAT WERE INVESTIGATED

<u>Code</u>	<u>Type</u>	<u>Trade Name</u>	<u>Manufacturer</u>
MC	Methylcellulose (15 cps)	Methocel [®]	The Dow Chemical Company Midland, Michigan
WE	Acrylic wax emulsion (B-60-A)	Rhoplex [®]	Rohm and Haas Philadelphia, Pennsylvania
PVA	Polyvinyl alcohol (40-20)	Gelvatol [®]	Shawinigan Resins Springfield, Massachusetts
HEC	Hydroxyethyl cellulose (WP-09)	Cellosize [®]	Union Carbide Chemical Co. New York, New York
PEG	Polyethylene glycol (4000)	Carbowax [®]	Union Carbide Chemical Co. New York, New York
CW	Tech. grade	Carnauba wax	Van Waters & Rogers, Inc. Denver, Colorado
TW	Embedding wax	Tissuemat [®]	Fisher Scientific Company
BW		Bees wax	Van Waters & Rogers, Inc. Denver, Colorado
PW	Type 1, Grade A	Paraffin	Denver Packaging Company Denver, Colorado

TABLE II

SAMPLES IMPREGNATED WITH WAXES

Time required to impregnate 3/4 inch by 3/4 inch samples with wax
at 250°F. and the tensile strengths of impregnated samples.

<u>*Wax</u>	<u>Time to Impregnate</u>	<u>Tensile Strength (psi)</u>
PEG	45 hr. (still not complete)	643
CW	7 hr.	649
TW	4 hr.	325
BW	21 hr.	192
PW	3 hr.	340

* See Table I for code.

TABLE III

TENSILE STRENGTHS OF UNFIRED ALUMINA SAMPLES

<u>Percent Binder</u>	<u>Number of Tests</u>	<u>Standard Deviation</u>	<u>Average Tensile Strength (psi)</u>
1.0 MC*, 0.2 glycerol	24	7.8	30.9
3.5 MC, 0.7 glycerol	24	8.4	88.7
1.0 MC	29	8.0	24.8
3.5 MC	46	10.6	73.3
1.0 MC, 1.0 PEG	44	4.3	44.4
3.5 MC, 1.0 PEG	38	6.5	71.5
2.0 WE	43	8.0	32.5
4.0 WE	42	12.3	52.4
1.0 WE, 0.3 MC	37	8.1	35.9
3.5 WE, 1.0 MC	36	11.9	98.0
1.0 HEC, 0.3 WE	22	9.9	30.0
3.5 HEC, 1.0 WE	17	16.6	77.2
1.0 PVA, 0.3 WE	31	6.3	28.9
3.5 PVA, 1.0 WE	37	11.0	70.9
1.0 HEC	10	5.9	20.7
3.5 HEC	33	14.4	83.0
1.0 HEC, 0.2 glycerol	25	5.7	29.1
3.5 HEC, 0.7 glycerol	25	15.0	90.9
1.0 HEC, 1.0 PEG	22	5.1	33.7
3.5 HEC, 1.0 PEG	37	12.0	85.4
1.0 PVA	20	13.0	43.3
3.5 PVA	25	19.0	132.2
1.0 PVA, 0.2 glycerol	18	6.6	29.6
3.5 PVA, 0.7 glycerol	30	16.2	124.3
1.0 PVA, 1.0 PEG	24	7.1	62.3
3.5 PVA, 1.0 PEG	36	12.0	123.1
4.5 MC, 1.0 WE	21	10.1	116.0

* See Table I for code.

TABLE IV

TENSILE STRENGTH OF UNFIRED OXIDES TEST BARS
WITH 4.0 PERCENT POLYVINYL ALCOHOL

Type of Ceramic	*Grain Size	Tensile Strength (psi)
85% alumina porcelain	-325 mesh	296.8
Alumina	-325 mesh	191.9
Magnesia	-200 mesh	150.5
Magnesia	2 microns	345.0
Zirconia	-200 mesh	167.2
Zircon	-400 mesh	227.5

* Before ball milling.

TABLE V

MACHINABILITY OF UNFIRED ALUMINA PARTS* COMPARED
TO THE TENSILE STRENGTH OF THE BINDER

Approximate (psi) Tensile Strength	Edges	Thread	Surface
60	badly chipped	rough	pock marked
100	badly chipped	rough	pock marked
140	sharp	rough	smooth
200	sharp	smooth	smooth
300	sharp	smooth	very smooth
650	sharp	very smooth	very smooth

* Alumina test part Figure 1

REVIEW OF LITERATURE

1. Levine, S., "Organic (Temporary) Binders for Ceramic Systems," *Ceramic Age*, No. 1, 39-42 (1960); and No. 2, 25-36 (1960).
2. Wild, A., "Review of Some Organic Binders for use in Structural Clay Products," *J. Am. Ceram. Soc.*, 33, No. 12, 368-70 (1954).
3. Thompson, J. J., "Forming Thin Ceramics," *J. Am. Ceram. Soc.*, 42, No. 9, 480-1 (1963).
4. Gormly, M. W., "Technical Aspects of Vitrified Grinding Wheel Manufacture: II, Materials and Compositions," *J. Am. Ceram. Soc.*, 37, No. 3, 144-7 (1958).
5. Wittemore, J. W., "Industrial Use of Plasticizers, Binders, and Other Auxiliary Agents," *J. Am. Ceram. Soc.*, 23, No. 11, 427-32 (1944).
6. Treischel, C. C., and Emrich, E. W., "Study of Several Groups of Organic Binders Under Low-Pressure Extrusion," *J. Am. Ceram. Soc.*, 29, No. 5, 129-32 (1946).
7. McNamara, E. P., and Comeforo, J. E., "Classification of Natural Organic Binders," *J. Am. Ceram. Soc.*, 28, No. 1, 25-31 (1945).

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