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BOEHMITE-BONDED HIGH-ALUMINA REFRACTORIES

by

GERHARD H. SCHIROKY, 1953-

A THESIS

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Approved by

Delbert E. Day (Advisor)

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BOEHMITE-BONDED HIGH-ALUMINA REFRACTORIES

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University of Missouri-Rolla, Rolla, Mo. 65401

ABSTRACT

High-alumina refractories (99+ % Al_2O_3) were produced by pressing a mixture of 70% tabular alumina and 30% reactive alumina and autoclaving in saturated steam at 1.4 MPa (200 psia)/194 °C to 3.4 MPa (500 psia)/242 °C for 12 to 96 h. Autoclaving converted the reactive alumina to boehmite which acted as the bond phase. At room temperature the MOR ranged up to 37 MPa depending upon boehmite content. The hot-MOR decreased steadily with increasing temperature, but was still 8 MPa at 1400 °C which exceeds that of comparable cement-bonded or conventionally fired high-alumina refractories. The estimated autoclaving costs are lower than conventional firing costs, but the overall economics of boehmite-bonded refractories are highly dependent upon the cost of the alumina used to form boehmite.

Based on a thesis submitted by G. H. Schiroky, University of Missouri-Rolla, for the M.S. degree in ceramic engineering, August 1979.

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I. INTRODUCTION

The strength of cement-bonded castables can increase considerably after an exposure to steam.[1-4] In a previous study[4], the modulus of rupture (MOR) of a high-alumina castable, bonded with a high purity calcium-aluminate cement, increased from 13 to 20 MPa after exposure to a saturated 47.5% steam/52.5% CO atmosphere at 199 °C and 3.21 MPa for the first six days. This increase in MOR was attributed to the formation of boehmite (AlO{OH}) during exposure.

The bonding provided by hydrothermally produced boehmite has been demonstrated in recent studies[5,6] of the mechanical properties of high-alumina bodies where the boehmite was developed by autoclaving reactive alumina in saturated steam at 205 °C for 16 h. The room temperature MOR, hot-MOR at 1400 °C, and crushing strength of these boehmite-bonded tabular alumina bodies were 7, 2.5, and 123 MPa, respectively.

Phase relations in the Al_2O_3-H_2O system have been studied by several authors.[7-12] Only diaspore and corundum can be considered stable phases. The metastable boehmite transforms under hydrothermal conditions above 300 °C reversibly to diaspore or corundum.[12]

The objective of this work was to investigate the feasibility of producing boehmite-bonded high-alumina refractories. The optimum autoclaving conditions, saturated steam pressure and exposure time, needed to produce a refractory with reasonable properties, were determined within assumed technological and economical limits. The mechanical and thermal properties of these high-alumina refractories containing no bond agent other than boehmite were measured and related to the autoclaving conditions. It was of particular interest to obtain strength data in the temperature regions where boehmite decomposes to γ-alumina (above 400 °C) and the γ-alumina eventually transforms ($\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$) into α-alumina. Therefore, the hot-MOR was measured between 25 °C and 1400 °C. The thermal expansion and firing shrinkage was measured to determine volume changes occuring during boehmite decomposition and after heating to higher temperatures. The room temperature MOR and porosity of autoclaved samples were measured and related to their boehmite content and microstructure.

II. EXPERIMENTAL PROCEDURES

A. Specimen Fabrication and Autoclaving Conditions

The kinetics of the alumina→boehmite reaction were investigated using two reactive alumina powders (RA-1* and RA-2*; for chemical and sieve analysis see Table I). Both powders were autoclaved simultaneously for 6, 12, 24, and 48 h in saturated steam at 0.41, 0.97, 1.52, and 2.07 MPa (60, 140, 220, and 300 psia; corresponding temperatures: 145, 178, 199, and 214 °C) in a stainless steel pressure vessel (2.5 cm in diameter, 4 cm high). The sealed vessel, containing the powders (in stainless steel crucibles) and water, was inserted into a furnace at the desired temperature, held at this temperature for the required time, and then removed. Approximately 1 h was required to heat and cool the vessel, but this time is not included in the exposure times.

Bars (8 by 1.8 by 1.5 cm) consisting of 30 weight % RA-2 and 70 weight % tabular alumina** (14 - 28 mesh = 25%; 28 - 48 mesh = 20%; -48 mesh = 25%; for chemical

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*RA-1 and RA-2 were A-3 and A-16 SG alumina, respectively, Aluminum Co. of America, Pittsburgh, Pa.

**T-61 tabular alumina, Aluminum Co. of America, Pittsburgh, Pa.

analysis see Table I), to which 10 weight % water was added, were pressed at 30 MPa. The proportions of reactive and tabular alumina and the particle size distribution of the tabular were chosen similar to those in a previous study[6]. Preliminary experiments showed that autoclaved bars containing RA-2 were stronger and less porous than those with RA-1, even though they contained less boehmite. Therefore, RA-2 was used in further experiments. The bars were dried (48 h at 105 °C), placed on a stainless steel stand above the level of distilled water in a carbon steel vessel[1], and then autoclaved in saturated steam at the pressures and times given in Table II. The desired steam pressure was reached after a heating time of roughly 10 h, which is not included in the autoclaving time. During exposure, the steam atmosphere was essentially static.

B. Property Measurements and Analysis Methods

The room temperature MOR was measured in 3-point bending* (5 cm span) using at least 10 samples to determine the average MOR.

The hot-MOR of bars autoclaved for 36 h at 2.76 MPa (400 psia)/229 °C was measured at 350, 460, 590, 750, 1000, 1400 °C in 3-point bending (5 cm span). Fourteen bars

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*Universal Testing Instrument TM-SM-L, Instron Corp., Canton, Mass.

were broken at each temperature after a 2 h soak according to ASTM-C-583 procedures. The heating rate averaged 150 - 200 °C/h.

The thermal expansion* was measured between 25 °C and 1000 °C at a heating rate of 250 °C/h. The shrinkage after firing and the porosity of selected samples was determined according to ASTM-C-113-74 and C-20-74, respectively.

Fracture surfaces of autoclaved bars were examined with a scanning electron microscope (SEM)** to acquire information about bonding and fracture mechanisms. The fracture surfaces of several bars fired at various temperatures were examined by SEM to see how the microstructure changed after thermal decomposition of the boehmite bond phase.

The boehmite content of one bar from each set of autoclaved specimens and the exposed alumina powders was determined by thermogravimetric analysis (TGA)***. A 400 mg sample was heated from room temperature to 900 °C at a heating rate of 10 °C/min and the amount of boehmite

*Automatic Recording Dilatometer, The Edward Orton Jr. Ceramic Foundation, Columbus, Oh.

**Scanning Electron Microscope Type JSM, Jeol Co., Japan

***TA-1 Thermoanalyzer, Mettler Instrument Corp., Highstown, N.J.

calculated from the weight loss occuring between 395 °C and 900 °C.

The crystalline phases present in the autoclaved powders and bars were identified by X-ray diffraction (XRD)*.

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*Kristalloflex 4, Siemens AG, West Germany

III. RESULTS

The quantity of boehmite formed in the alumina powders increased with exposure time and steam pressure, as shown in Fig. 1. Fig. 2 shows that more boehmite was formed in RA-2 than in RA-1 for short exposure times, but at longer exposure times the reverse was true. The tabular alumina powder (-325 mesh) showed no detectable conversion to boehmite during exposure to the same conditions.

The MOR, porosity, and boehmite content (c_b) of autoclaved bars made with RA-2 alumina are listed in Table II. The right hand column of Table II, q, gives the percentage of reactive RA-2 alumina converted to boehmite and shows that complete conversion (q = 100%) was not achieved for these autoclaving conditions. Complete conversion to boehmite corresponds to $c_b = 33.5\%$.

The change in room temperature MOR and c_b with increasing steam pressure is shown in Fig. 3. In Fig. 4 the MOR is seen to increase at first linearly with t, but then becomes constant with longer exposure times. The boehmite content changes similarly, whereas, the porosity decreases steadily. The change in hot-MOR is shown in Fig. 5.

The boehmite content of different bars from the same exposure differed only by ±3%. The boehmite content of bars from two separate exposures, but at nominally the same conditions, differed at most by ±10%. This is most likely due to the slight differences in the heating rate of the autoclave and slight fluctuations in the steam pressure occuring during operation.

The typical thermal expansion of an autoclaved bar containing 16.7% boehmite is shown in Fig. 6. The volume increase occuring between 500 °C and 600 °C is due to the decomposition of boehmite and its magnitude is proportional to the boehmite content, see Appendix E. The firing shrinkage of autoclaved bars initially containing 16.7% boehmite is listed in Table III.

The porosity of bars, autoclaved at different conditions, decreased linearly with increasing boehmite content, see Fig. 1 in Appendix B.

IV. DISCUSSION

A. Strength of Autoclaved High-Alumina Refractories

The formation of boehmite from RA-2 was the only reaction found in the autoclaved bars by XRD, SEM, and TGA. As shown in Figs. 3 and 4, the increase in MOR generally paralleled the change in boehmite content. This correlation between the MOR and boehmite content is illustrated further in Fig. 7, where the autoclaving conditions are ignored and the MOR is compared directly with c_b. It is concluded from this correlation that the boehmite formed from the reactive alumina is the bonding phase responsible for the strength increase. This conclusion is supported by the results of other studies[1-6].

Boehmite single crystals formed from reactive alumina during autoclaving have a rhombohedral shape. The (001) face with its characteristic angles[13] of 76° and 104° is generally larger than the (110) faces, as can be seen for the boehmite crystals in Fig. 8 A. The strength imparted by the boehmite results from its microstructure of interlocking crystals. The boehmite crystals form twins and grow together (coalesce), as shown in Fig. 8 A and Fig. 9. Fig. 9 D, G, H, and K show how excellently the tabular alumina grains are imbedded in the boehmite bond phase.

The photomicrographs of Fig. 9 generally show that fracture of autoclaved bars occurs between the tabular alumina grains and the bond phase, as illustrated in Fig. 9 A. The smooth surface of the bond phase shows that it was in good contact with the tabular alumina (Fig. 9 A and E). The bond phase may even be pulled out of the pores of the tabular alumina grains (Fig. 9 C through G), but not always, (Fig. 9 B).

B. Development of the Boehmite Bond Phase

The general model for the development of the bonding provided by boehmite is as follows. After pressing the agglomerated reactive alumina particles fill the voids between the coarse tabular alumina grains and may even penetrate voids within the grains. This structure is shown schematically in Fig. 10 A and B. For the reasons given below it is believed that boehmite formation starts on the surface of these agglomerates (Fig. 10 C) and moves progressively into the bulk. First, steam can penetrate the pores of a pressed sample and come into contact with the surface of the agglomerates easier than it can diffuse into the bulk of the individual particles. Second, the density of boehmite[14] (3.01 g/cm^3) is lower than that for α-alumina (3.98 g/cm^3), so additional volume is required for the growth of boehmite crystals. This volume can be better provided at the agglomerate surface, such that adjacent pore volume is filled as is consistent with the observed reduction in porosity, Fig. 4. Third, the fracture surfaces shown in Fig. 9 F and L appear to consist of 100%

boehmite, but from TGA it is known that in this sample only 48.5% of the RA-2 was converted to boehmite. Finally, the kinetics of boehmite formation from reactive alumina as found in this and other studies[5] suggest a surface type reaction.

The four curves in Fig. 1 A indicate three regions of boehmite formation: a nucleation region, a region where the rate of boehmite formation is high, and a region where the rate is low. When the logarithm of c_b is plotted against the logarithm of t (Fig. 1 B), a proportionality between ln c_b and ln t can be seen for 0.41 MPa. At higher steam pressures ln c_b is only initially proportional to ln t . After some time ln c_b increases more slowly, but as one can see clearly for 2.07 MPa, is again proportional to ln t. Similar results from another study[5] were explained by assuming that after nucleation boehmite formation proceeds by a surface-type reaction which eventually becomes dependent upon bulk diffusion.

The kinetics of boehmite formation shown in Fig. 1 B are described by

$$c_b = A \times (t)^{n_i} \tag{1}$$

where

c_b = boehmite content of exposed reactive alumina

A = constant

t = exposure time

n_i = exponent which is pressure and time dependent

One has to differentiate between n_i for a surface-type reaction, n_s, and that for a diffusion-type reaction, n_d. From the slopes of the curves in Fig. 1 B, the calculated values for n_s are about 0.7 to 1.4 and for n_d about 0.3.

The values for n_s and n_d of a reactive alumina used in a recent study[5], measured at 1.72 MPa, are 2 and 0.3, respectively. For the same pressure the values for RA-1 are $n_s \approx 1.4$ and $n_d \approx 0.3$, and for RA-2 $n_s \approx 0.7$ and $n_d \approx 0.2$. The specific BET-surface areas of RA-1 and RA-2 were measured to be 11 and 9 m^2/g, respectively, whereas that for the cited reactive alumina is reported[5] to be 54 m^2/g. The purest alumina is RA-2, followed by RA-1, Table I, whereas for the cited reactive alumina a Al_2O_3-content of only 98% is given[6]. It follows, that n_s increases with increasing specific surface area. A smaller particle size facilitates boehmite formation initially (RA-2 forms more boehmite than RA-1 for short exposure times, Fig. 2), but for longer exposure times a higher specific surface area and/or a higher impurity content enhances boehmite formation. (For long exposure times RA-2 forms less boehmite than RA-1, Fig. 2. A 16 h exposure to saturated steam at 205 °C (1.7 MPa) caused a transformation of 82% of the reactive alumina in the cited study[5], compare with Fig. 2).

In the recent study[5] it was shown that the surface reaction rate is thermally activated. An activation energy of 71 kJ/mol was reported. Activation energies between 70 and 80 kJ/mol for RA-1 and RA-2 were found in this investigation. An increase of n_s with higher saturated steam pressure is therefore reasonable, because more activation energy is provided for the boehmite formation, when the temperature increases.

To summarize, it is believed that boehmite formation starts on the surface of the reactive alumina agglomerates, which fill the voids between the coarse tabular alumina grains. The kinetics of boehmite formation can be described with a parabolic law. Reactive aluminas with a higher specific surface area and a higher content of impurities seem to form boehmite more readily.

C. Properties of Autoclaved Bars

1. Modulus of Rupture

As shown in Fig. 4, the MOR initially increases with exposure time and then levels off, becoming independent of boehmite content, Fig. 7. In Fig. 7 the MOR becomes constant when about 48.5% of the RA-2 alumina has been converted to boehmite. The error bars in Fig. 7 specify a region, in which the average MOR-value would be expected for a different set of specimens autoclaved at the same condition.

This leveling off of the MOR is also consistent with the interpretation of a surface-type reaction. One can assume that at a certain degree of conversion the surface of the reactive alumina agglomerates is covered with boehmite crystals. As shown schematically in Fig. 10 E, further boehmite formation within the bulk of the particles need not provide any further bonding. Interestingly, the MOR-curve levels off at essentially the same time corresponding to the inflection point in the c_b-curve in Fig. 4, where the rate of boehmite formation commences to decrease.

2. Hot-Modulus of Rupture

The approximately 50% decrease in flexural strength between room temperature and 400 °C is attributed in a general way to the dehydration of boehmite which according to TGA starts at ∿400 °C and reaches a maximum at ∿550 °C. The small subsequent change in hot-MOR above 400 - 500 °C as the boehmite transforms to γ-alumina is attributed to the pseudomorphous character of these two phases. As can be seen in Fig. 8 A, B, C, and D, the gross external shape of boehmite is preserved in γ-alumina. According to Ervin[15], the basic atomic arrangement of boehmite is almost undisturbed in changing to γ-alumina.

Various authors[16,17] report a transformation of γ- to δ-alumina between 700 °C and 900 °C and of δ- to Θ-alumina between 900 °C and 1000 °C. The Θ to α transformation is reported to occur at about 1200 °C. Because of the similarities of the structures of γ-, δ-, and Θ-alumina and the topotaxy of the γ to δ and δ to Θ transformations, it is reasonable that no significant decrease in the hot-MOR occurs throughout these transitions. The shape of the supposedly δ-alumina crystals in Fig. 8 E is similar to that of boehmite. Above 1200 °C α-Al_2O_3 commences to recrystallize by preferred orientation[17] (rhombohedral shaped α-alumina crystals like those of boehmite can be seen in Fig. 8 F), therefore no noticeable decrease in strength occurs at this temperature. After 48 h at 1550 °C, the α-alumina crystals have partly developed their equilibrium faces and sintered together (Fig. 8 G, H, and I). The former (001) faces of boehmite can hardly be detected.

Positive identification of the transition alumina phases by XRD was difficult because the weak γ-, δ-, and Θ-alumina peaks are partly superimposed by the strong α-alumina peaks (from the tabular alumina) and partly superimpose each other. After firing at 700 °C, 1000 °C, and 1400 °C, however, weak γ- and δ-alumina peaks, and those of α-alumina only, respectively, were recorded.

3. Thermal Expansion and Firing Shrinkage

The thermal expansion coefficient for α-alumina increases with temperature, but the curve in Fig. 6 is convex below 500 °C and above 750 °C. This might be due to the expansion behavior of the bond phase. Bugosh[18] pressed bars from fibrous colloidal boehmite, which showed shrinkage during heating between room temperature and 450 °C. He further reported the bars, consisting after boehmite dehydration of γ-alumina, to shrink while heated from 600 °C to 1000 °C.

The dashed lines in Fig. 6 show how the linear expansion due to the boehmite dehydration, which was proportional to the boehmite content (Appendix E), can be determined graphically. Since the densities[14] of boehmite and γ-alumina are 3.01 and 3.2 g/cm^3, respectively, and the shape of the crystals does not seem to change during the dehydration of boehmite to γ-alumina, the increase in volume between 500 °C and 600 °C is somewhat unexpected. This volume increase is currently unexplained.

No permanent dimensional changes of significance were apparent after firing to 1000 °C, see Fig. 6 and Table III. The densities[14] of γ-, δ-, Θ-, and α-alumina are 3.2, 3.2, 3.56, and 3.98 g/cm^3. The formation of Θ- and α-alumina could account for the 0.5% linear shrinkage after firing to 1225 °C. The continued formation of α-alumina and sintering are the probable causes of the 1.2% shrinkage after firing for 48 h at 1550 °C.

4. Porosity

No changes in the external dimensions of the specimens were observed after autoclaving. The conversion of the α-alumina in RA-2 to boehmite with its larger specific volume would logically produce a decrease in porosity as was observed, Fig. 4. Likewise, firing the autoclaved specimens caused a slight increase in porosity, Table II, as the boehmite was reconverted to the higher density α-alumina. Because of the firing shrinkage, the porosity after firing was lower than that after pressing, Table II.

D. Comparison of Boehmite-Bonded and other High-Alumina Refractories

1. Properties

The measured properties of boehmite-bonded high-alumina refractories are equal or superior to those of commercial cement-bonded high-alumina castables or fired high-alumina refractories. Unlike a castable, the boehmite-bonded material consists after firing of at least 99% Al_2O_3 and should therefore be suitable for application at higher temperatures. As no dimensional changes occur during autoclaving and as the firing shrinkage is not too large, Table III, the dimensions of boehmite-bonded shapes at high temperatures would be close to those after pressing.

Even though the boehmite-bonded specimens undergo a volume increase between 500 and 600 °C, their general expansion behavior is not appreciately different from that of a similar, cement-bonded high-alumina castable (70% tabular alumina* and 30% cement*), as shown in Fig. 6. Unlike the castable, which generally shows a permanent

*T-61 tabular alumina of similar particle size graduation and CA-25 cement, Aluminum Co. of America, Pittsburgh, Pa.

shrinkage after heating, the dimensional changes for the boehmite-bonded sample after heating to 1000 °C were negligible.

The room temperature-MOR (after heating to 104 °C) and hot-MOR of a commercial high alumina (97.0% Al_2O_3 and 2.7% CaO)[19] castable* are compared with the boehmite-bonded refractory in Fig. 5. The strength of the boehmite-bonded material is not only substantially higher than that for this castable, but even exceeds that of conventionally fired high-alumina refractories (hot-MOR of a 99.5% Al_2O_3 material[20] with 21% porosity: 2.8 MPa at 1350 °C; for a 99.4% Al_2O_3 material[21] with 26% porosity: 3.4 MPa at 1350 °C).

The application of boehmite-bonded high-alumina refractories seems feasible in terms of their mechanical and thermal properties.

2. Cost

Firing costs for normal high-alumina refractories are up to 50 $/ton[22], while the estimated cost for the autoclaving process for producing boehmite-bonded high-alumina refractories is between 1 and 5 $/ton. Due to rapidly increasing energy costs this difference in manufacturing costs is likely to increase considerably in the future.

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*Castable #141A, C-E Refractories, Combustion Engineering Inc., Valley Forge, Pa.

Using current (July 1979) raw material prices, the raw material costs for a refractory composed of 70% tabular alumina and 30% RA-2, RA-1, or cement* were calculated to be \$ 694, 467, and 486 per ton, respectively. Obviously, the cost of the reactive alumina used to form boehmite is an important factor to the total raw material cost. A lower cost, less pure material than the RA-2 used in this study might be preferable if the impurities enhance its conversion to boehmite.

With a cheaper reactive alumina than the one used in this investigation, the production of boehmite-bonded high-alumina refractories could be economically feasible.

*CA-25 cement, Aluminum Co. of America, Pittsburgh, Pa.

V. SUMMARY

Boehmite-bonded high-alumina refractories were produced by pressing a mixture of 70% tabular and 30% reactive alumina and autoclaving in saturated steam at 1.4 to 3.4 MPa (194 to 242 °C) for 12 to 96 h. During autoclaving, the reactive alumina reacted with steam to form boehmite which comprised the bond phase. Boehmite formation started on the surface of the reactive alumina agglomerates, which fill the voids between the coarse tabular alumina grains. The MOR of autoclaved bars increased proportionally to the boehmite content (measured by TGA) and then leveled off at 37 MPa, where 48.5% of the reactive alumina had been converted to boehmite. At this point the surface of the reactive alumina agglomerates consisted completely of boehmite, i. e., anywhere between reactive and tabular alumina were boehmite crystals. Inspite of continued boehmite formation no further boehmite crystals came into contact with the tabular alumina grains. Because the autoclaved bars fractured at the tabular alumina/boehmite interface, no further increase in strength was observed.

The porosity, MOR, hot-MOR, thermal expansion and firing shrinkage are equal or even superior to those of commercial high-alumina products. The production of boehmite-bonded high-alumina refractories may be economically feasible, especially in view of the rapidly increasing energy costs. The cost of autoclaving is lower than firing costs for high-alumina materials. A less expensive reactive alumina which forms a strong boehmite bond phase would result in a substantial reduction in estimated cost.

TABLE I

CHEMICAL AND SIEVE ANALYSIS OF ALUMINAS (WEIGHT PERCENT)*

	RA-1	RA-2	Tabular Alumina
Chemical Analysis			
Al_2O_3.......%	99.0	99.5+	99.0+
SiO_2........%	0.02	0.02 - 0.04	0.06 - 0.2
Fe_2O_3.......%	0.04	0.01 - 0.02	0.06 - 0.08
Na_2O........%	0.45	0.05 - 0.09	0.10
Sieve Analysis			
on 100 mesh...%	4 - 15		
on 200 mesh...%	50 - 75		
on 325 mesh...%	88 - 98		
thru 325 mesh...%	2 - 12	99 - 100	

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*Product Data Chemicals, Calcined, Reactive, Tabular Aluminas and Calcium Aluminate Cement, Sect. GA2A, April 1976, Aluminum Co. of America, Pittsburgh, Pa.

TABLE II

MOR, APPARENT POROSITY AND BOEHMITE CONTENT AS A FUNCTION OF AUTOCLAVING CONDITIONS

pressure (MPa)	exposure time (h)	MOR[§] (MPa)	porosity[§] (%)	c_b (%)	q[†] (%)
1.38	36	7.2 ± 1.9	20.6 ± 0.8	6.0	17.2
2.07	24	23.1 ± 4.8	18.7 ± 0.7	12.2	35.1
2.76	12	25.0 ± 3.5	19.0 ± 0.5	13.0	37.6
2.76	24	30.4 ± 4.5	17.4 ± 1.4	14.2	41.0
2.76	36	36.9 ± 1.8	16.1 ± 1.3	16.7	48.5
2.76	36		18.2 ± 0.7*		
2.76	48	36.3 ± 3.7	15.2 ± 0.3	19.8	58.0
2.76	96	36.9 ± 2.9	14.0 ± 1.3	22.3	65.5
3.45	24	36.6 ± 6.9	15.3 ± 0.6	16.7	48.5
			22.7 ± 0.6**		

§: ± represents standard deviation

†: percentage of RA-2 which reacted during the exposure with steam to boehmite

*: porosity of autoclaved bars after firing for 48 h at 1550 °C

**: calculated porosity of bars after pressing (see Appendix B)

TABLE III

PERCENT LINEAR SHRINKAGE AFTER FIRING FOR BARS AUTOCLAVED FOR 36 h AT 2.76 MPa

firing conditions		shrinkage after firing
time	temperature	
48 h	1000 °C	0.1 %
48 h	1225 °C	0.5 %
48 h	1550 °C	1.2 %

FIGURE CAPTIONS

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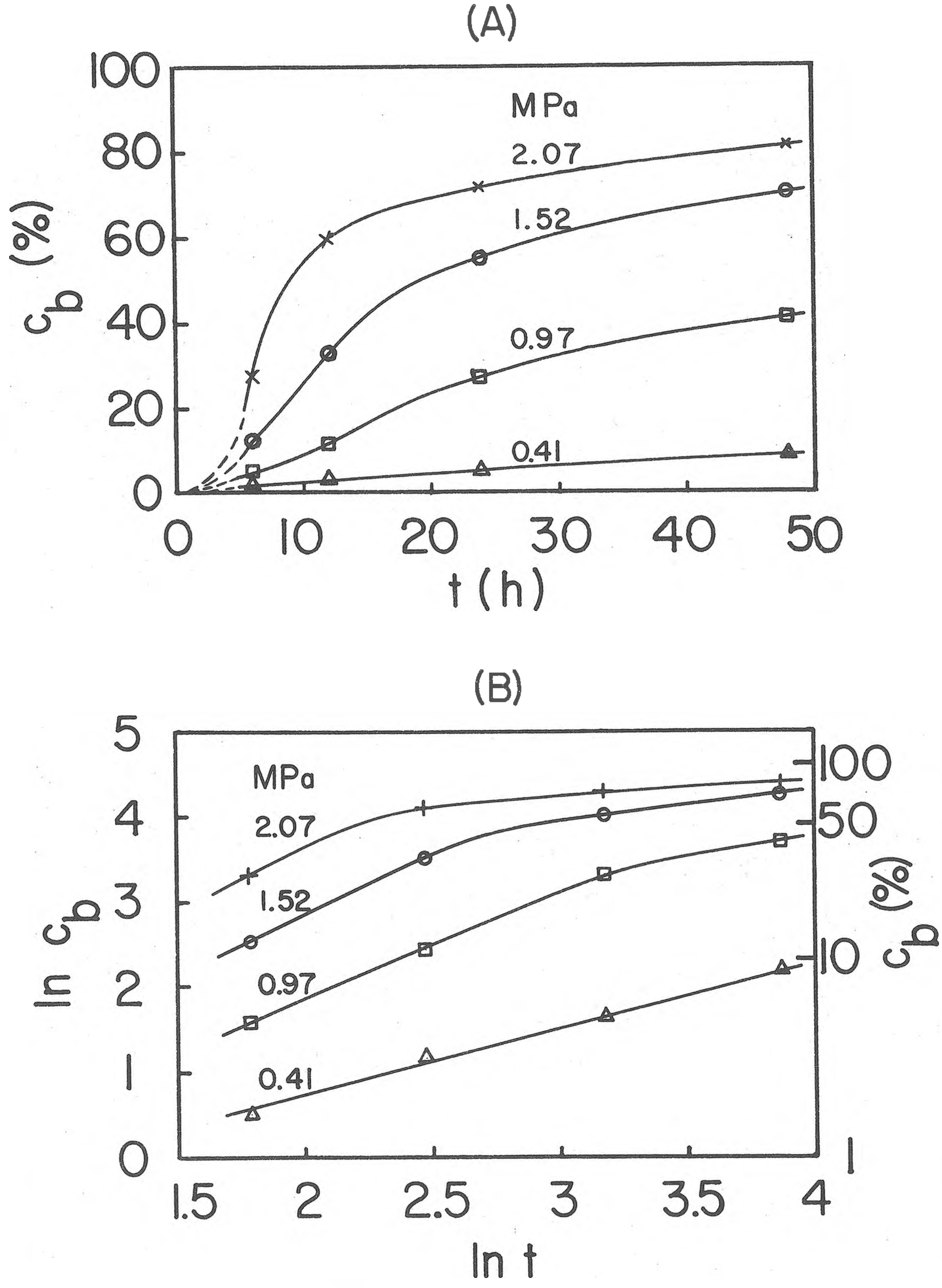
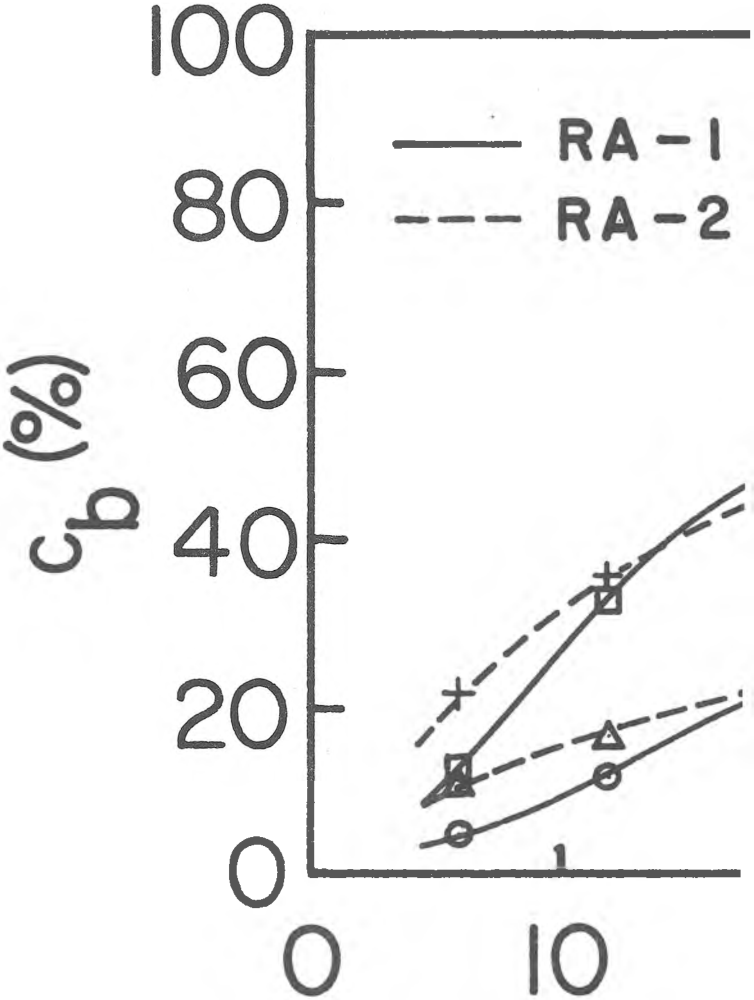

(A)
100
80
60
40
20
0
c_b (%)
MPa
2.07
1.52
0.97
0.41
0
10
20
30
40
50
t (h)
(B)
5
4
3
2
1
0
ln c_b
MPa
2.07
1.52
0.97
0.41
100
50
10
1
c_b (%)
1.5
2
2.5
3
3.5
4
ln t

Fig. 1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60
40
20
0
c_b (%)
RA-1
RA-2
0
10

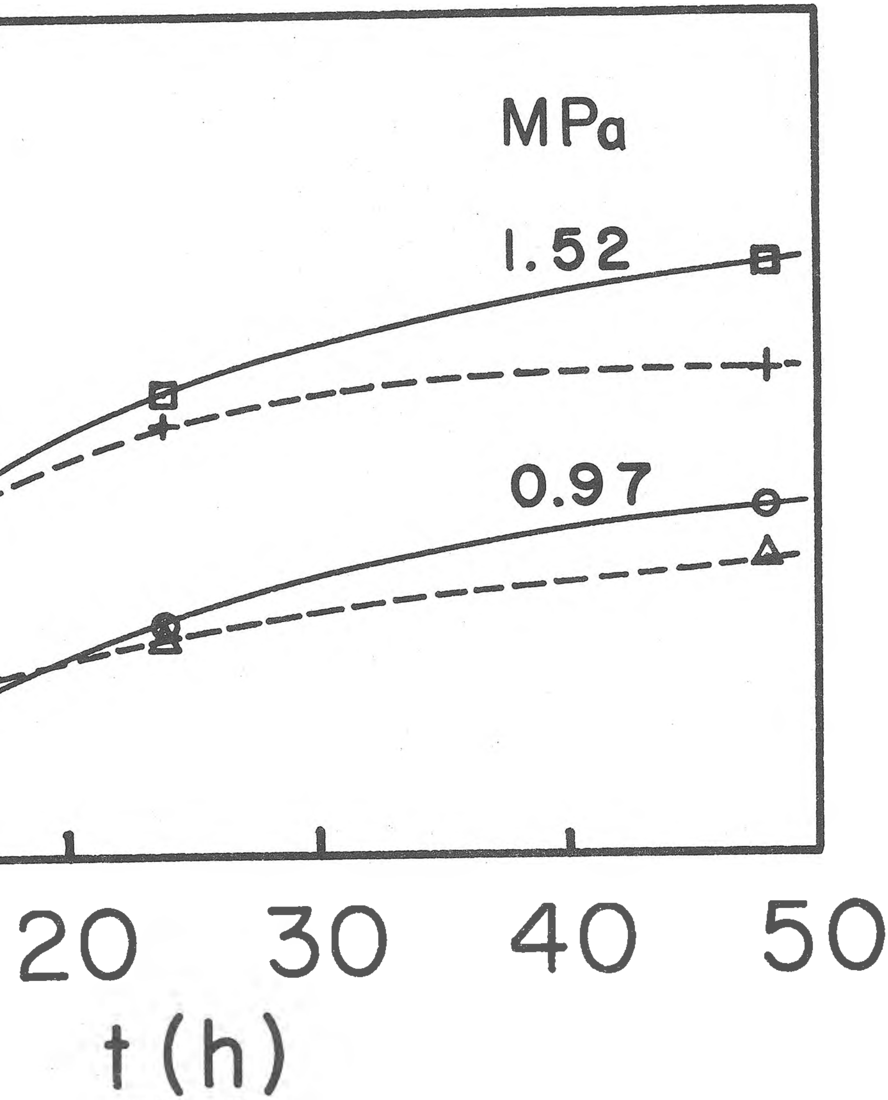
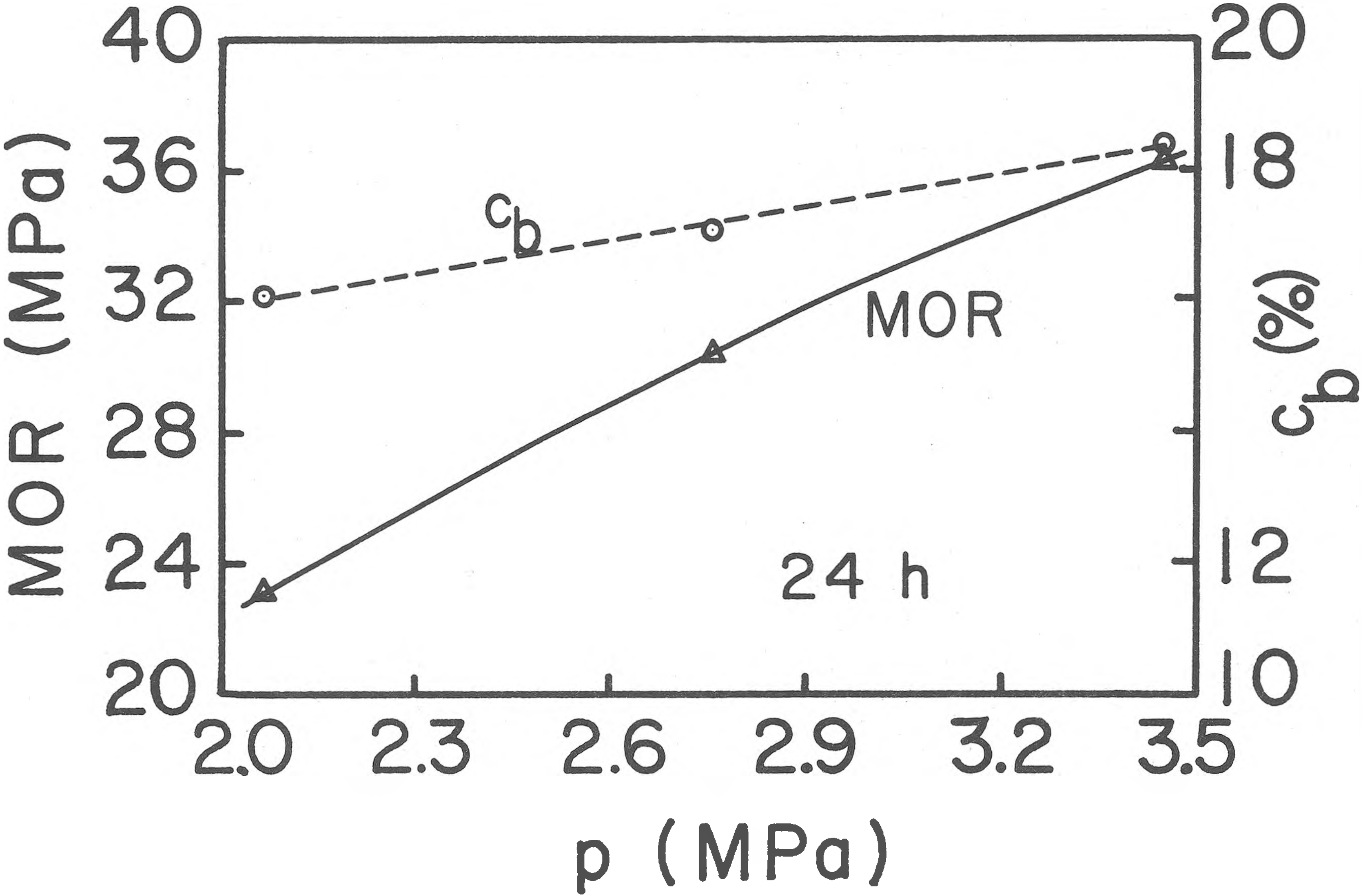


Fig. 2



MOR (MPa)
40
36
32
28
24
20
c_b (%)
20
18
12
10
2.0
2.3
2.6
2.9
3.2
3.5
p (MPa)
c_b
MOR
24 h

Fig. 3

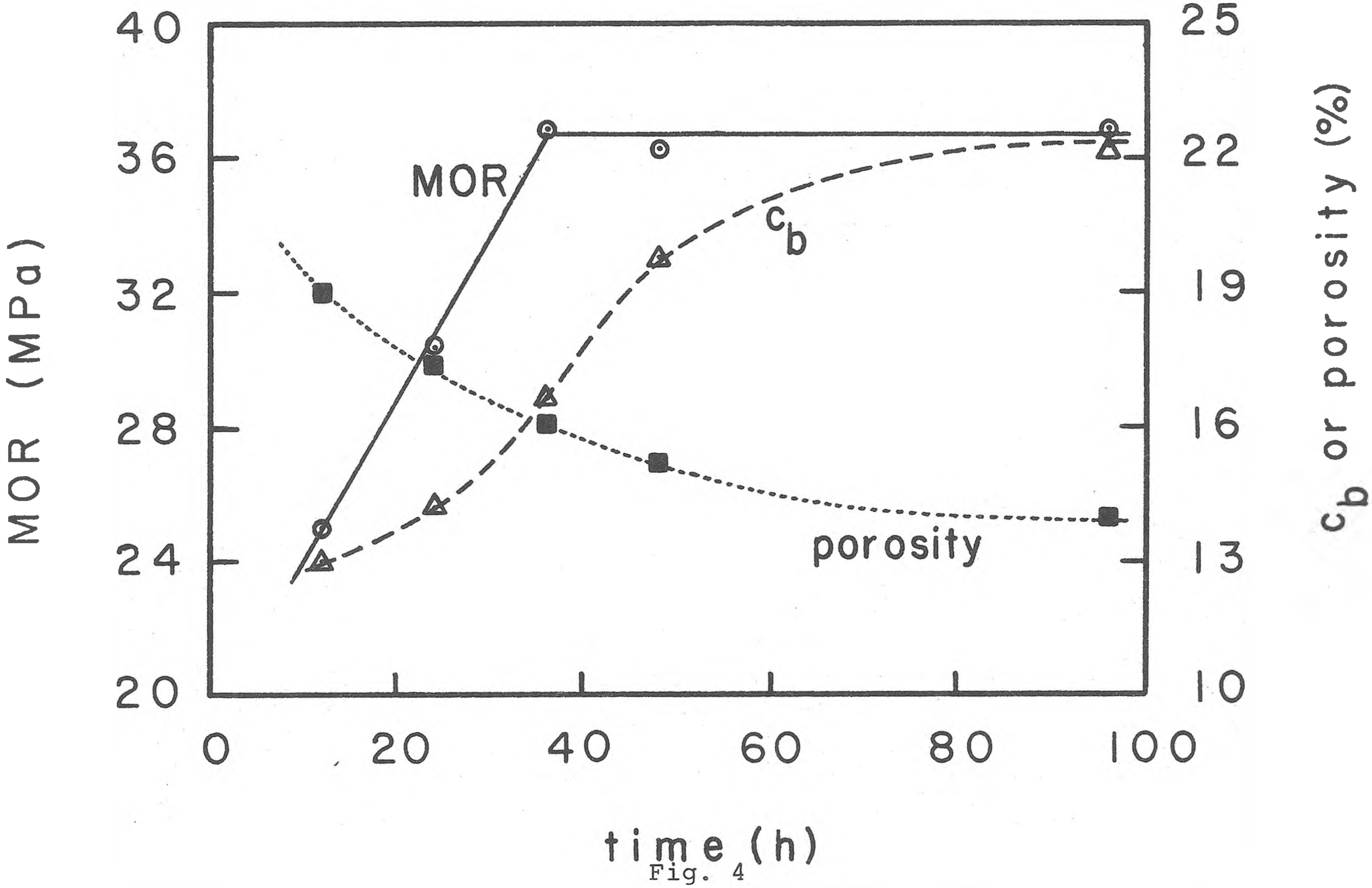

MOR (MPa)
40
36
32
28
24
20
0
20
40
60
80
100
25
22
19
16
13
10
c_b or porosity (%)
MOR
c_b
porosity
time (h)

Fig. 4

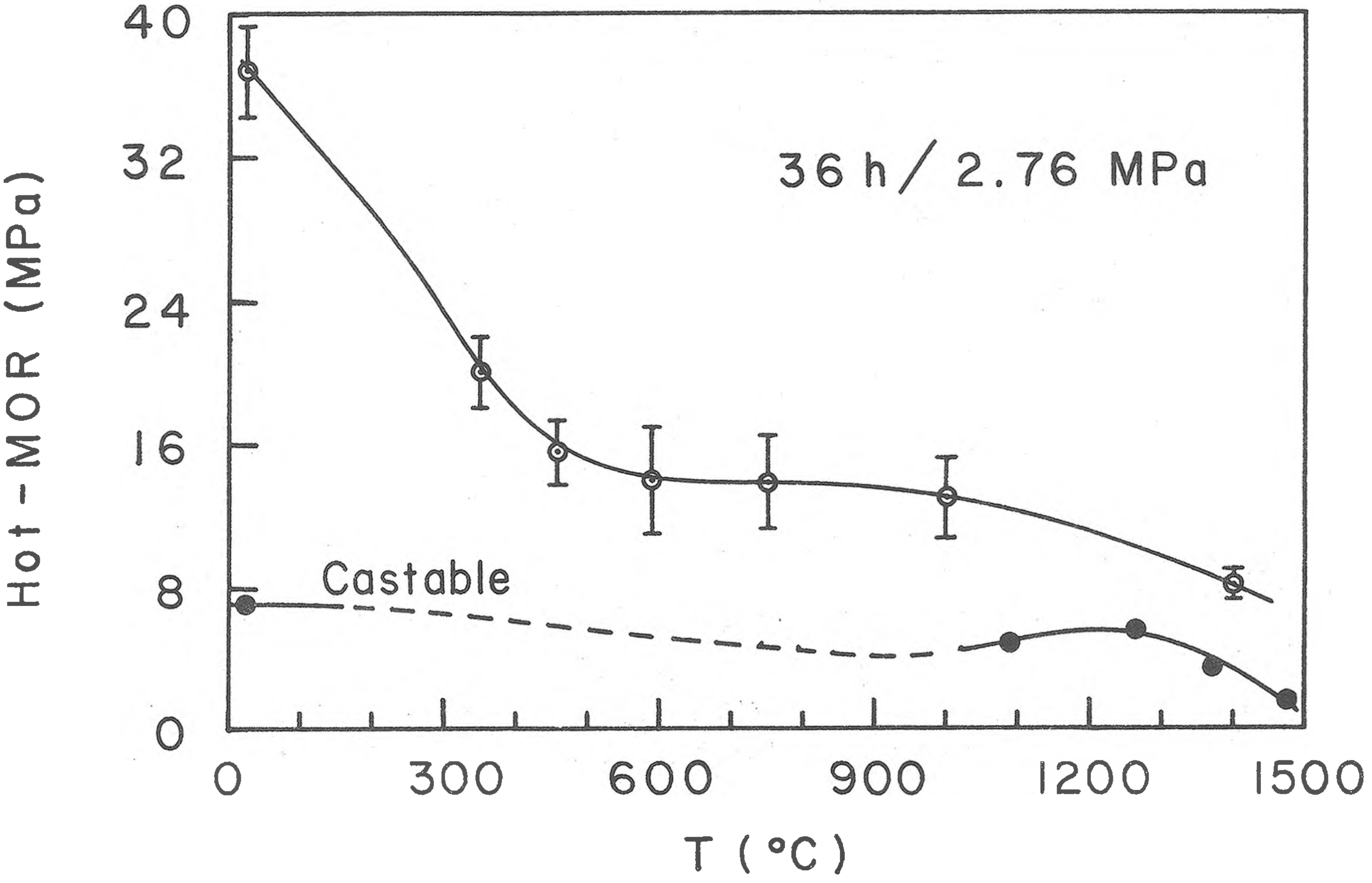

40
32
24
16
8
0
Hot - MOR (MPa)
36 h / 2.76 MPa
Castable
0
300
600
900
1200
1500
T (°C)

Fig. 5

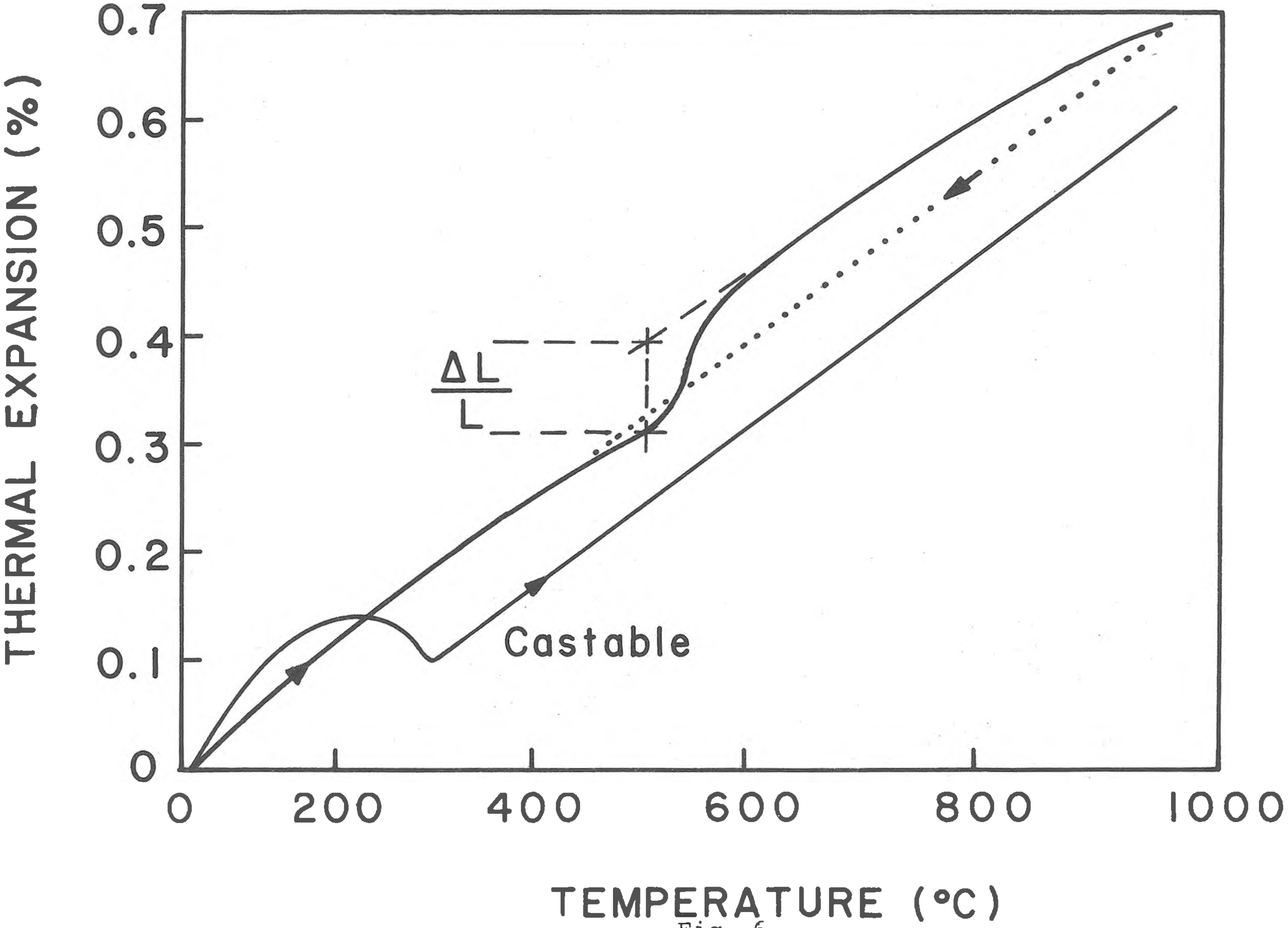
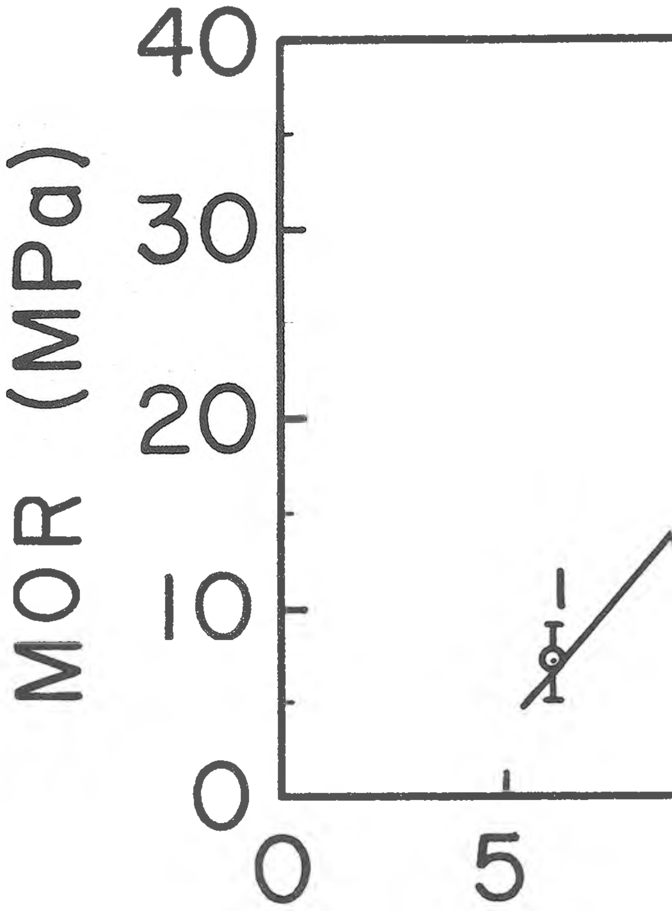

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
THERMAL EXPANSION (%)
$\frac{\Delta L}{L}$
Castable
0
200
400
600
800
1000
TEMPERATURE (°C)

Fig. 6


MOR (MPa)
40
30
20
10
0
0
5

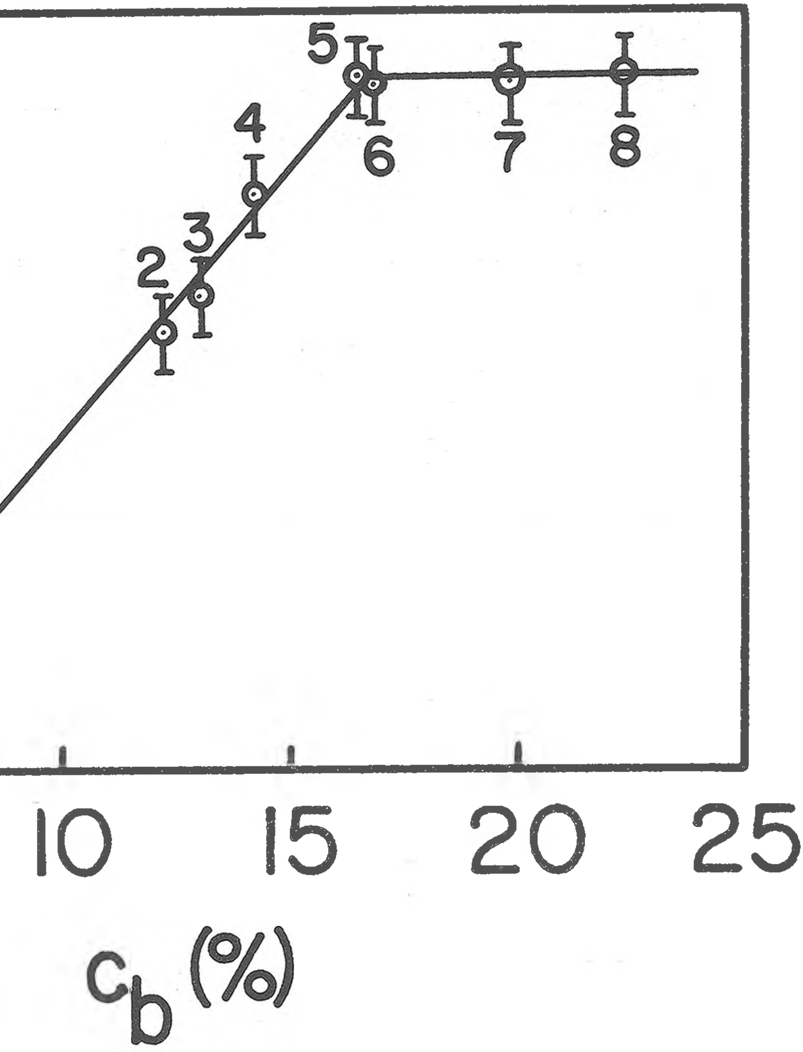


Fig. 7

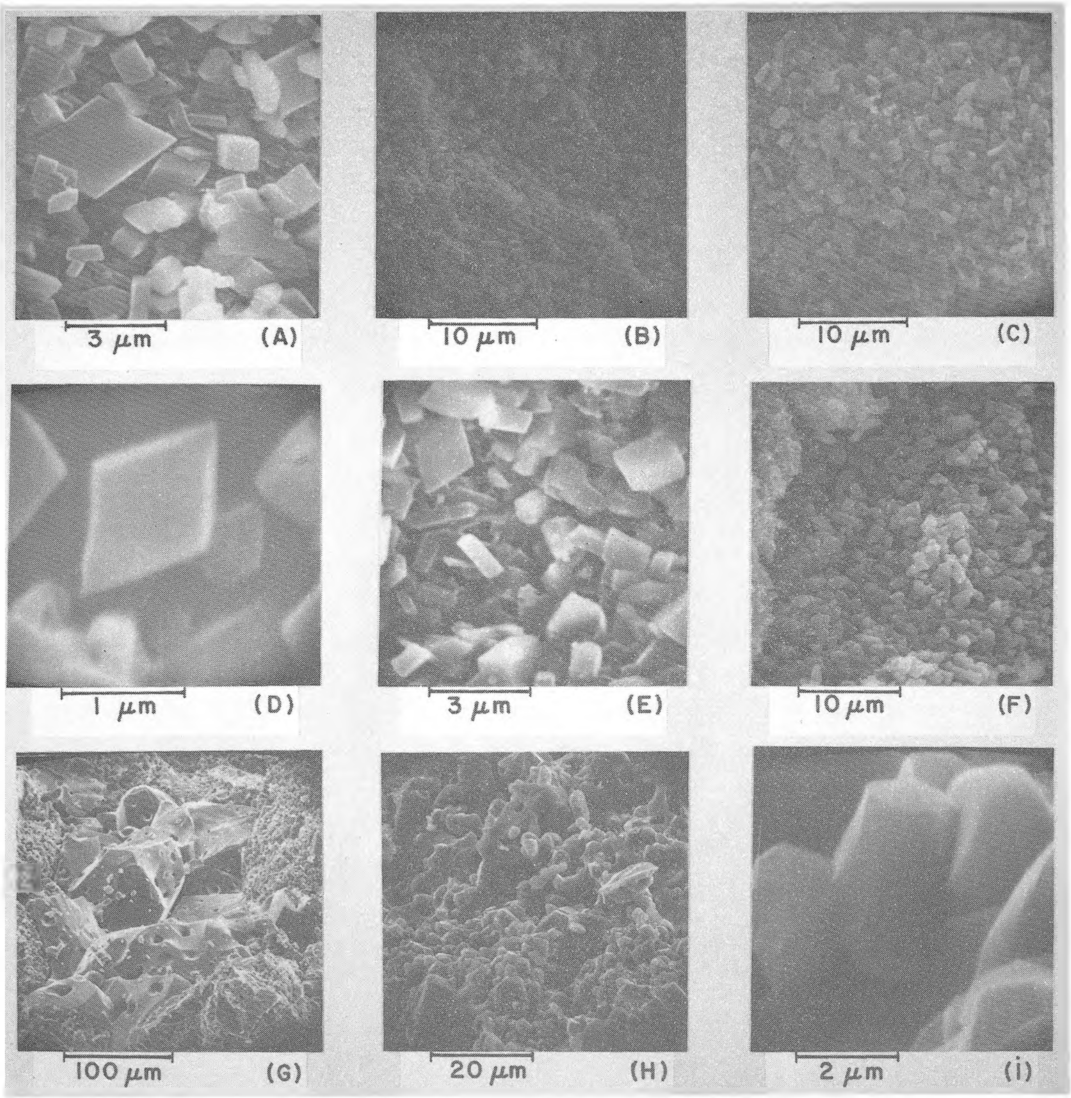


Fig. 8

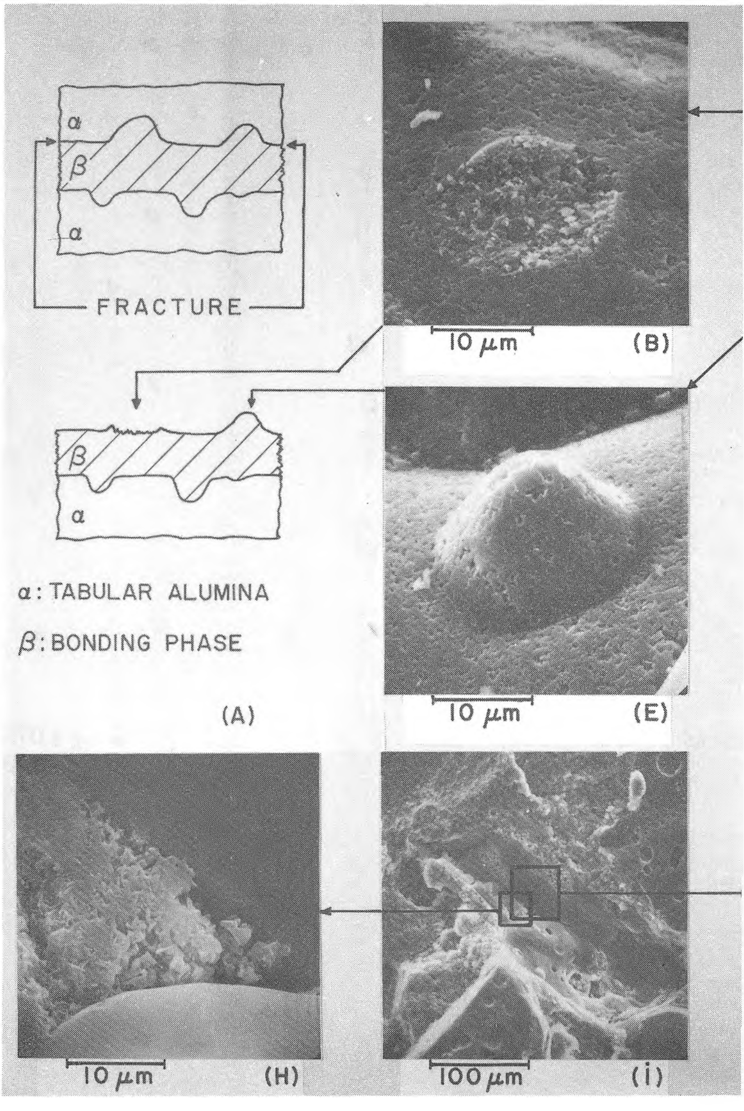
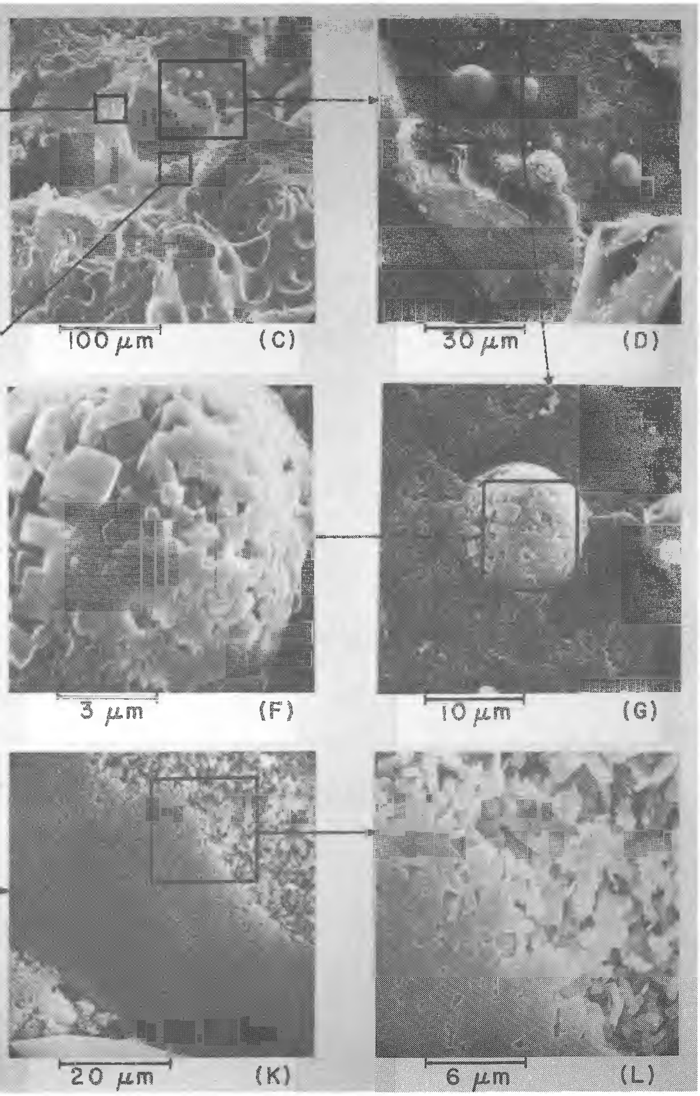
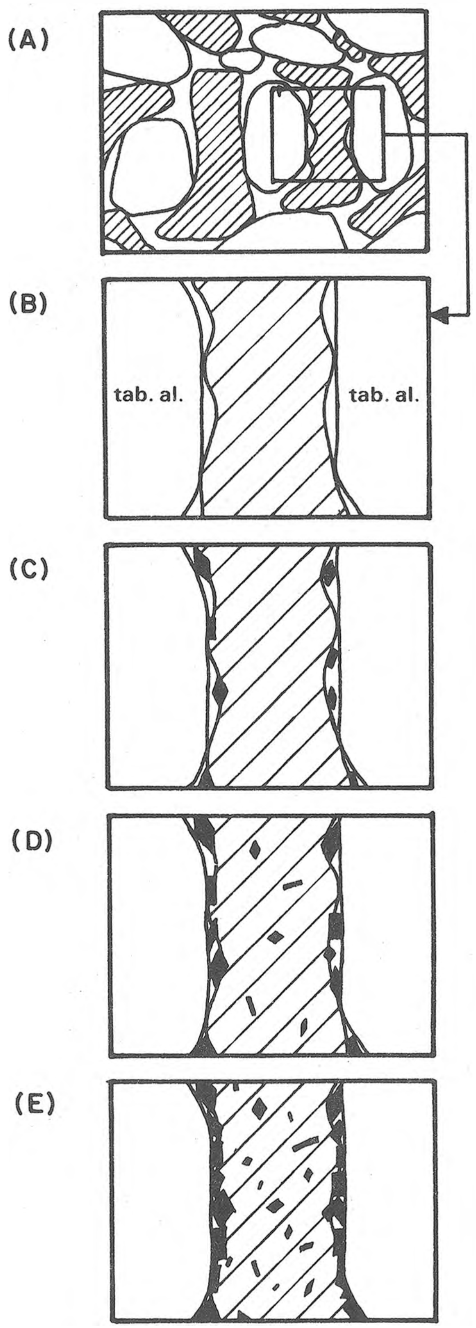

α
β
α
FRACTURE
β
α
α: TABULAR ALUMINA
β: BONDING PHASE
(A)
10 µm
(B)
10 µm
(E)
10 µm
(H)
100 µm
(i)

Fig.



9

DEVELOPMENT OF THE BOEHMITE BONDING PHASE



The reactive alumina particles (each consisting of many crystallites) agglomerate during the pressing process.

Reactive alumina agglomerate between two tabular alumina (tab. al.) grains.

Boehmite crystals growing on surface of agglomerate.

Growth of existing boehmite crystals and formation of new crystals within agglomerate (between particles).

Continued formation of boehmite within agglomerate, which provides no additional bonding.

Fig. 10

ACKNOWLEDGEMENT

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VITA

Gerhard Hans Schiroky was born on October 1, 1953 in Nuernberg, Western Germany. He studied Materials Science from September 1973 to March 1978 at the Friedrich-Alexander Universitaet Erlangen-Nuernberg. After passing his diploma examinations he has been enrolled in the Graduate School of the University of Missouri-Rolla since April 1978. He held a research assistantship from the Graduate Center for Materials Research for the period April 1978 to July 1979.

APPENDICES

APPENDIX A

CALCULATION OF THE PERCENTAGE OF REACTIVE ALUMINA CONVERTED TO BOEHMITE DURING AUTOCLAVING

Known from TGA: weightloss w of sample with

weight m_{TGA}

$$\underset{102}{Al_2O_3} + \underset{\underset{w}{18}}{H_2O} \longrightarrow \underset{\underset{m_b}{120}}{2\ AlOOH}$$

$$m_b = 6.67 \times w \tag{1}$$

Weight before autoclaving: $M = m_{TGA} - w$ (2)

Weight of tabular alumina: $m_{TAB} = 0.7 \times M$ (3)

Weight of reactive alumina converted to boehmite: $m^*_{Al} = m_b - w$ (4)

Weight of reactive alumina unconverted to boehmite: $\bar{m}_{Al} = m_{TGA} - m_{TAB} - m_b$ (5)

Weight of reactive alumina: $m_{Al} = m^*_{Al} + \bar{m}_{Al}$ (6)

Percentage of reactive alumina converted to boehmite:

$$q = \frac{m^*_{Al}}{m_{Al}} \times 100\% = 18.9 \times \frac{w}{m_{TGA} - w} \times 100\% \tag{7}$$

Percentage of boehmite in reactive alumina after autoclaving:

$$r = \frac{m_b}{\bar{m}_{Al} + m_b} \times 100\% = \frac{6.67 \times w}{0.3 \times m_{TGA} + 0.7 \times w} \times 100\% \tag{8}$$

Boehmite content of sample:

$$c_b = \frac{m_b}{m_{TGA}} \times 100\% = \frac{6.67 \times w}{m_{TGA}} \times 100\% \tag{9}$$

APPENDIX B

CALCULATION OF THE POROSITY OF SAMPLES AFTER PRESSING FROM BOEHMITE CONTENT AND POROSITY OF THE SAMPLES AFTER AUTOCLAVING AT A CERTAIN PRESSURE-TIME CONDITION

The calculation is made under the assumption that during autoclaving the linear dimensions of the samples remain unchanged.

Mathematically: $$v_p^* + v_a^* + v_b^* = v = \text{const} \qquad (1)$$

v : volume of sample

v_p^*: volume of pores

v_a^*: volume of alumina

v_b^*: volume of boehmite

The following abbreviations are used:

v_p : volume of pores in autoclaved sample
v_a : volume of alumina in -"-
v_b : volume of boehmite in -"-
m_a : weight of alumina in -"-
m_b : weight of boehmite in -"-
m : weight of -"-
c_b : boehmite content of -"-
p : porosity of -"-
d : density of -"-
m_o : weight of pressed (unautoclaved) sample
p_o : porosity of -"-
d_o : density of -"-

d_a : density of alumina

d_b : density of boehmite

We want to calculate p_o. We write: $p_o = 1 - \frac{d_o}{d_a}$ (2)

d_o can be expressed using the relation: $d_o = \frac{m_o}{v}$ (3)

from (2) and (3):

$$p_o = 1 - \frac{m_o}{v \times d_a} \quad (4)$$

To find an expression for $\frac{m_o}{v}$, we write:

$$v_p + v_a + v_b = v \quad (5)$$

$$\frac{v_p}{v} = p \quad (6)$$

(5) and (6):

$$\frac{v - (v_a + v_b)}{v} = p \quad (7)$$

$$1 - \frac{1}{v} \times (v_a + v_b) = p \quad (8)$$

$$1 - \frac{1}{v} \times \left(\frac{m_a}{d_a} + \frac{m_b}{d_b}\right) = p \quad (9)$$

$$m_a = (1 - c_b) \times m \text{ and } m_b = c_b \times m \quad (10)$$

$$1 - \frac{m}{v} \times \left(\frac{1 - c_b}{d_a} + \frac{c_b}{d_b}\right) = p \quad (11)$$

m has to be expressed in terms of m_o. Only part of the alumina in the pressed sample will react during the exposure to boehmite. Therefore we can write:

$m_o = m_{Al_2O_3}$(will not react) + $m_{Al_2O_3}$(will react)

From the boehmite content of the autoclaved sample we can calculate how much alumina reacted:

$$\begin{array}{lcl} \mathrm{Al_2O_3} + \mathrm{H_2O} & \longrightarrow & 2\ \mathrm{AlOOH} \\ 102 & & 120 \\ x & & m_b \end{array} \qquad x = 0.85\times m_b \qquad (12)$$

Therefore: $m_o = m_a + 0.85\times m_b$ (13)

Using equation (10) and rearranging leads to:

$$m = \frac{m_o}{1 - 0.15\times c_b} \qquad (14)$$

Substituting for m in equation (11) and rearranging gives:

$$1 - \frac{m_o}{v} \times \left(\frac{d_b + (d_a - d_b)\times c_b}{d_a\times d_b - 0.15\times d_a\times d_b\times c_b} \right) = p \qquad (15)$$

Substituting for $d_a = 3.98$ and $d_b = 3.01$:

$$1 - \frac{m_o}{v} \times \left(\frac{3.01 + 0.97\times c_b}{11.98 - 1.80\times c_b} \right) = p \qquad (16)$$

Let C represent the term in brackets in equation (16).

With equation (3): $d_o = \frac{m_o}{v} = \frac{1 - p}{C}$ (17)

With equation (2): $p_o = 1 - \frac{d_o}{d_a} = 1 - \frac{1 - p}{d_a\times C}$ (18)

Substitution for $d_a = 3.98$:

$$p_o = 1 - \frac{1 - p}{3.98\times C} \qquad (19)$$

The calculated porosities of pressed samples are shown below:

p_{st} (MPa)	t (h)	c_b (%)	C	p (%)	p_o (%)
1.38	36	6.0	0.2584	20.6	22.8
2.07	24	12.2	0.2660	18.7	23.2
2.76	12	13.0	0.2670	19.0	23.8
2.76	24	14.2	0.2685	17.4	22.7
2.76	36	16.7	0.2716	16.1	22.4
2.76	48	19.8	0.2755	15.2	22.7
2.76	96	22.3	0.2786	14.0	22.5
3.45	24	19.8	0.2716	15.3	21.6

p_{st} : saturated steam pressure
t : exposure time

Average p_o-value and standard deviation: 22.7 ± 0.6 %. This is in excellent agreement to the p_o-value of 22.6 % obtained by extrapolating the curve in Fig. 1 to $c_b = 0$.

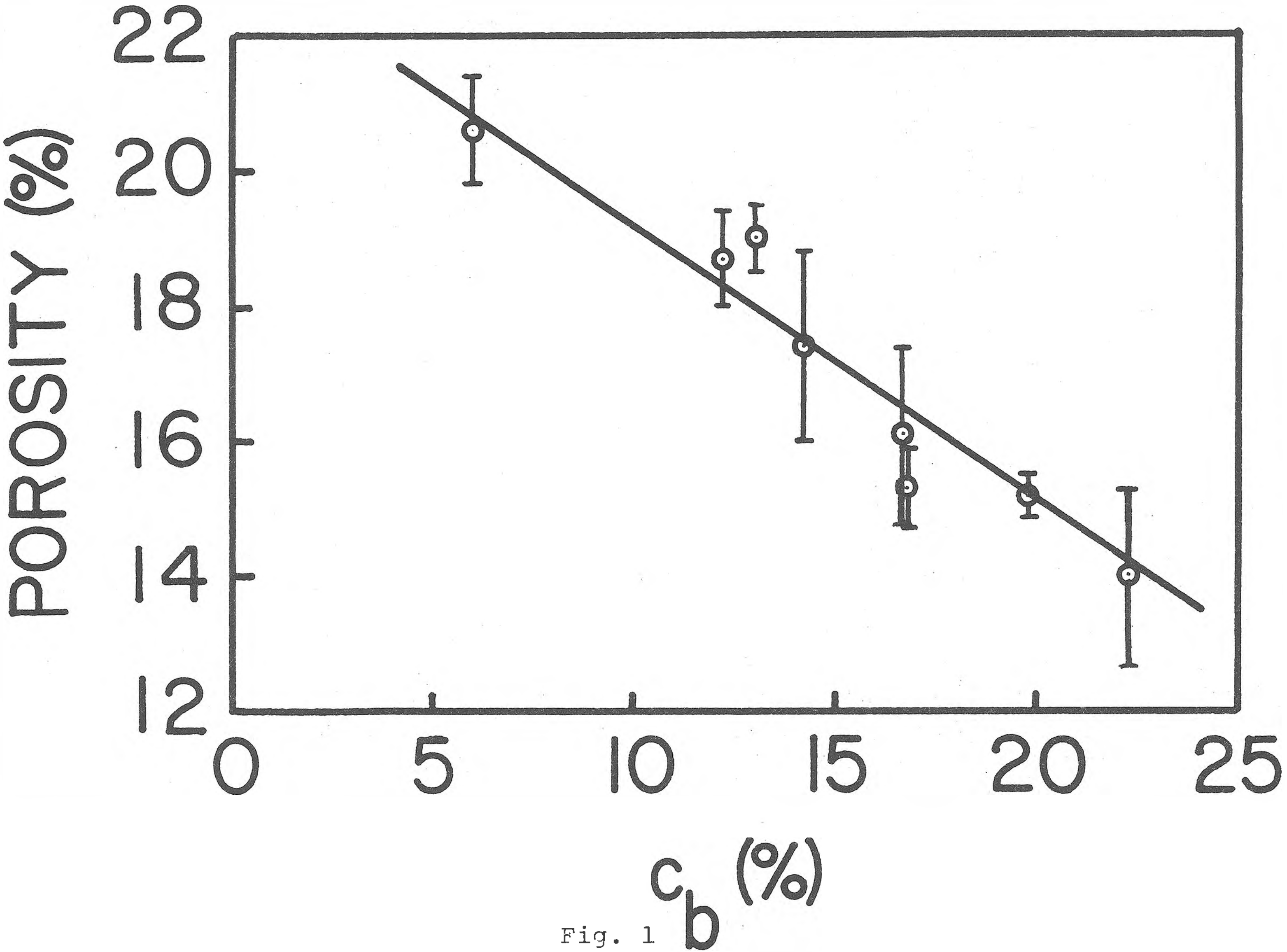

Fig. 1
Porosity of autoclaved bars versus boehmite content

APPENDIX C

HOT-MODULUS OF RUPTURE

Temperature (°C)	hot-MOR* (MPa)
25	36.9 ± 2.5
350	20.0 ± 2.0
460	15.6 ± 1.8
590	14.0 ± 2.9
750	13.9 ± 2.6
1000	13.0 ± 2.2
1400	8.2 ± 0.8

*Average of 14 specimens. Plus and minus limits are standard deviation.

APPENDIX D

BOEHMITE CONTENT OF ALUMINA POWDERS (RA-1 AND RA-2) AFTER AUTOCLAVING AS DETERMINED BY TGA

time (h)	6	12	24	48	powder
pressure (MPa)					
0.41	1.7	3.2	5.2	8.8	RA-1
	5.3	7.2	8.0	8.5	RA-2
0.97	4.8	11.5	27.3	41.4	RA-1
	11.3	16.5	26.3	35.2	RA-2
1.52	12.5	33.2	55.0	70.5	RA-1
	21.8	35.7	51.2	57.9	RA-2
2.07	27.7	59.9	72.0	81.2	RA-1
	38.7	54.2	58.0	69.9	RA-2

APPENDIX E

VOLUME INCREASE OF BOEHMITE-BONDED SPECIMENS DUE TO BOEHMITE DEHYDRATION

The dashed lines in Fig. 6 show how the linear expansion during heating due to the boehmite dehydration was determined graphically. This value multiplied with 3 gives the volume expansion, which is proportional to the boehmite content in the bars, as can be seen in Fig. 1.

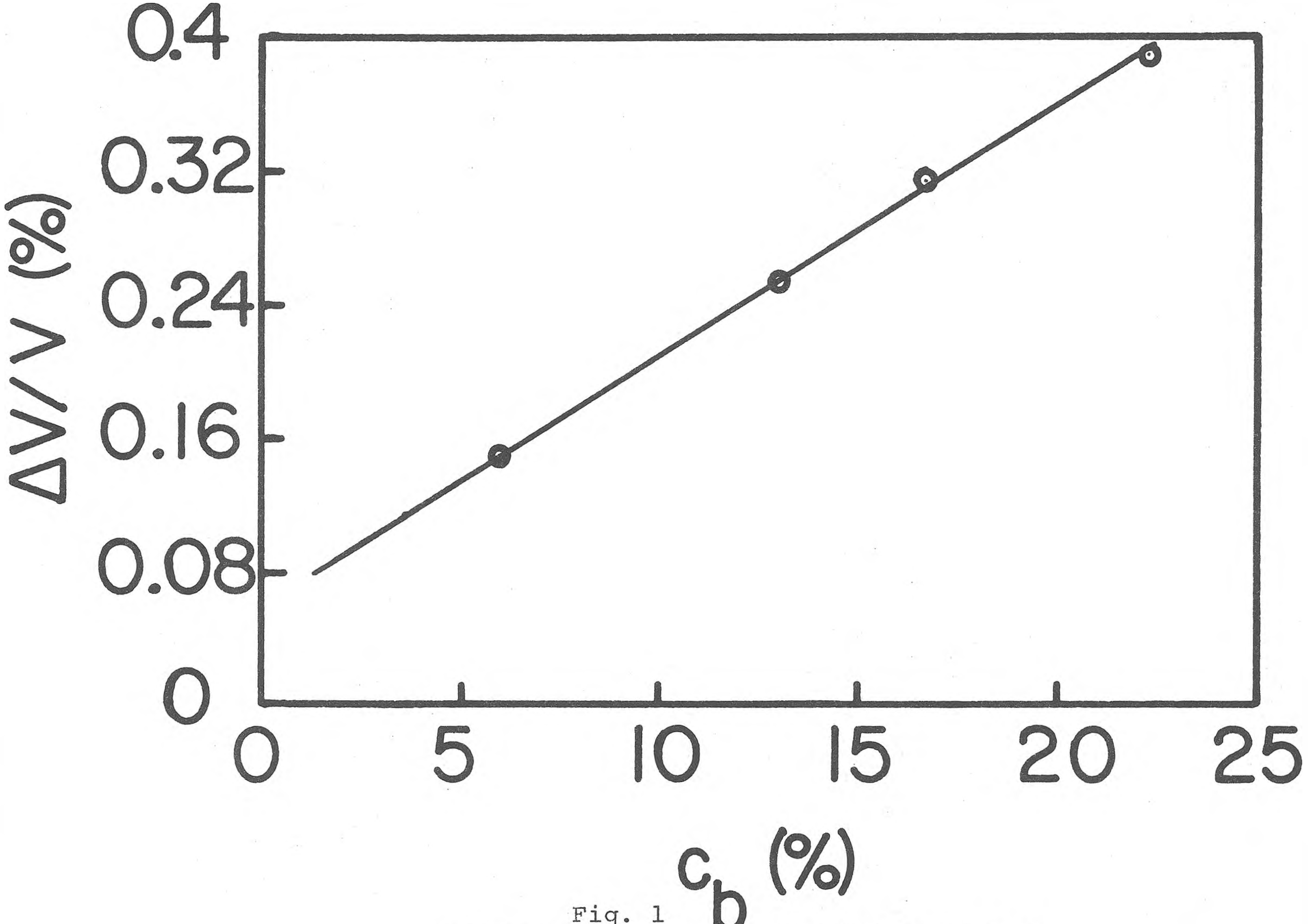

Fig. 1
Volume increase versus boehmite content