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SECOND ANNUAL REPORT

THE ROLE OF ANIONS IN MECHANICAL FAILURE

Submitted by

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Metallurgical Engineering
and
Materials Science

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COLLEGE OF ENGINEERING
UNIVERSITY OF KENTUCKY

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ON THE

ROLE OF ANIONS IN MECHANICAL FAILURE

Submitted by

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ABSTRACT

Studies have been conducted involving the fabrication and proper-ties of hot-pressed polycrystalline magnesium oxide containing anion impurities. The impurities planned for use were sulfur, fluorine, chlorine, hydroxyl and deuterated hydroxyl. Considerable difficulty was encountered in preparing specimens doped with deuterium because of exchange with hydrogen. Attempts to date have been unsuccessful and results for such specimens are not included. Property studies include fabrication, grain growth, microhardness and diffusion. Results involving fabrication of MgO in the presence of anions indicate that sulfur and chlorine are very detrimental to the densification process, apparently by formation of volatile gas products. Fluorine and hydroxyl have slightly detrimental effects, although not as severe as the sulfur and chlorine.

Grain growth studies indicate these anion impurities, in general, do not inhibit grain growth, in fact, specimens containing porosity exhibited grain growth rates comparable to those found with pore-free undoped material. Many phases of the work, including microhardness and chemical analysis, suggest that the solubility of chlorine and sulfur in MgO is extremely low, while fluorine and hydroxyl may remain in the specimens during exposure to high temperatures at more substantial levels.

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INTRODUCTION

The purpose, scope and justification for these studies of anion impurities in ceramic materials is extensively discussed in the first annual summary report (Ref. 1). Very briefly, the work encompasses the fabrication of anion doped magnesium oxide by hot pressing (which includes the effect of anions on the fabrication), grain growth, grain boundary diffusion and microhardness. Chemical analysis of such anions is included, however, extensive development of analytical procedures is not. As in all prior reports the results are subdivided into subsections, each concentrating on a single phase of the program.

The further understanding of the importance of anions in mechanical behavior of ceramics should include actual strength testing. Such work does form a later part of this program and is now being initiated. A new subsection to include such studies is introduced in this report.

SECTION 1

FABRICATION

The studies of fabrication in this research fulfill two needs:
1) to make available suitable specimens containing anion impurities,
and 2) determination of the effect of these impurities on the fabrication.
The materials, methods and equipment used are all discussed in
prior reports (Ref. 1).

The major process variable studied in the fabrication of the anion
doped material has been temperature. Hot pressing pressure has been
held at 13,000 psi and specimens have been held at maximum temperature
and pressure until no further movement of the press ram was detectable
in five minutes (less than 0.0005 inches). Specimen size for these studies
has been 3/4" diameter by approximately 3/8" thick. A curve of the data
for each anion and the undoped MgO is shown in Figs. 1-5 and a summary
plot in Fig. 6. The lines shown are least square linear fits and are pre-
sented for convenience and not to propose a linear relationship. Although
originally five anions were planned for study, attempts to fabricate MgO
which is doped with OD have been unsuccessful and data for it are not
included. This is discussed more thoroughly under Section 5, Chemical
Analysis.

The most general feature exhibited by the curves in Fig. 6 is re-
duction of density accompanying introduction of any anion impurities. The
order of decreasing effect on reduction of density is $Cl \sim S < F < OH <$ un-
doped and dehydrated. Since the undoped material is known to contain OH
in amounts of the order of 1 at%, difference between it and OH doped may be
considered an indication of the effect of variations in amount. The dehy-
drated material is closer to a "pure" standard, but still certainly contains
some volatile species. It was prepared by either vacuum calcining at
300°C and .1 torr and by dry box handling or washed with absolute ethyl
alcohol just prior to pressing.

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The process by which these volatile impurities interfere with densification, as well as their exact location in the MgO lattice, is, of course, of considerable interest. If the impurities are in solution within the lattice, the question arises whether they would preferentially segregate at the grain boundaries or remain uniformly distributed throughout the crystallites. In the latter case one would expect their effect on densification to be small. If the impurities are not capable of solution within the MgO lattice, they would normally be expected to exist as precipitates. However, because of the volatile nature of the impurities, either in the elemental state or in the form of compounds of magnesium, the possibility exists for entrapped gas phase within the microstructure. Either precipitates or gases would result in retardation of the densification processes and lower observed densities. These various possibilities may be considered in light of the known physical characteristics of the anion impurities to ascertain which one has the greatest likelihood of controlling.

Table 1 shows the vapor pressures and ion sizes of the species of concern here. If one assumes that the anion impurities are not held within solution in the MgO lattice, then one would expect that the effect on densification of each of these anions would rank with the appropriate vapor pressures. That is, $OH > Cl > S \geq F$ for the compounds and $F > Cl > OH > S$ for the elements. Since neither of these is consistent with the first observed behavior ($S \sim Cl > F > OH$), one concludes that the vapor pressure of the volatile species is not the only factor of concern.

One may next consider the solubility of each of these anion impurities in the MgO lattice. Detailed studies of the solubility limits of these species in MgO have not been found. Phase diagrams, when available, do not show solubility limits and in many cases are not available. Consequently, consideration of the anion size in substitution

for oxygen in MgO suggests that fluorine and hydroxyl would show reasonable solubility while chlorine and sulfur would not. Such a conclusion is based on the assumption that the bond configuration does not change with such substitution, which would appear to be reasonable in a highly ionic material like MgO. It also assumes that charge balance may be maintained by association of anion impurities with cation impurities or with magnesium defects. Other workers have shown such behavior(Ref.2). Using the simple ionic size model for the solubility of these impurities with MgO the rank of effect on densification would be $S \sim Cl > F \geq OH$. This rank is quite close to the one actually observed, the only consistency being that fluorine impurities are more deterimental than hydroxyl, rather than approximately equal. If the fluorine and hydroxyl are both indeed in solution, a difference in their location within the lattice (grain boundary versus the interior) may account for the observed difference in behavior.

On the basis of this analysis, one does conclude that chlorine and sulfur are not held in solution in magnesium oxide but are rejected to form either precipitate particles or entrapped gas. The levels of these impurities which are maintained after hot pressing are consistent with this conclusion (see Section 5). However, it would be further desirable to know whether the rejected anion species form second phase particles within the MgO which inhibit sintering or whether they exist as in entrapped gas creating high pressure pores. To date this point has been unresolved. Optical examination does not reveal second phase particles, however, in the presence of substantial porosity small amounts could easily be undetected. Work is planned to extend the resolution by using the scanning electron microscope, but to date has not been completed.

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SECTION 2

GRAIN GROWTH

Further study on the effect of different anions on grain growth kinetics of MgO has been done. The effect of Cl^-, F^- and S^{-2} has been studied at 1300°C and 1500°C while OH^- was studied at 1500°C only. The reheat times varied from 1 hour to about 200 hours. The reheat was done in a platinum resistance furnace with a temperature control of $\pm$ 20°C and with an air atmosphere.

The preparation of samples for grain size measurements straight-forward. They were cold mounted and polished on diamond through a 6μ wheel. For a finer polish a 1μ Al_2O_3 cloth wheel was used and for a good grain definition, a final 0.3μ Al_2O_3 polish was used. Grain boundaries were etched in a solution of two parts 85% H_3PO_4 and one part 70% H_2SO_4 at room temperature. The time for etching depended on the average grain diameter expected, which was directly related to the reheat time. A 2-minute etch gave good results for reheat times of about 10 hours, while a time of 5 minutes was needed for 100 hour reheats. The average grain sizes were determined by the linear intercept method. This method is described in some detail (Ref. 1) in the earlier report.

Table 2 gives a list of the as-pressed densities and the dopant concentration in the different samples and the grain growth data are given individually and in summary in Figs. 7-12. The grain growth data thus far obtained are still under study and no complete conclusions can be made at this time. However, on comparing our results with that of other investigators it is clear that anion impurities do not inhibit grain growth. (See Figs. 11 and 12.) At 1300°C the grain sizes for doped MgO in this work are definitely larger than that for undoped MgO, both in the work of Spriggs (Ref. 3) and Gordon (Ref. 4). This is in spite of the fact that these samples contained as much as 4% porosity while Spriggs, et al. worked with pore-free transparent MgO and Gordon, et al. reported porosity from 0.1 to 0.4%. At 1500°C this work also showed a larger grain size than Gordon et al.

and was comparable to that of Spriggs. Daniels, et al. (Ref. 5), working with undoped MgO of about the same porosity as in this work, reported considerable smaller grain sizes.

Observations of the data for each dopant are not necessarily complete but are summarized below. In Fig. 9 (sulfur dopant), at $1500^{\circ}C$, all three samples gave a slope close to one-third for log D vs log t curve verifying that a cubic grain growth law is obeyed, namely:

$$D_t^3 - D_o^3 = Kt \text{ where } K = \text{ rate constant.}$$

This is in accordance with that obtained by Daniels, et al. (Ref. 5) for porous MgO. The as-pressed sample had a porosity of about 4%. The reason for the difference in level of the curve for sample 96 compared to samples 30 or 33 at $1500^{\circ}C$ is not clear at this point but may perhaps be traced to the different amounts of sulphur dopant added. At $1300^{\circ}C$ sample 96 showed a slope close to one-half, which is for square grain growth kinetics as predicted by Spriggs (Ref. 3) for transparent, dense MgO, rather than the lower one-third seen in the other curves. This is as yet unexplained.

Grain growth in chlorine doped MgO at $1500^{\circ}C$ (See Fig. 8) showed a rapid decay in the rate of growth after 10 hours. This sample has as much as 5% porosity and at $1500^{\circ}C$ the pores were trapped within the grains. For $1300^{\circ}C$ the pores were observed primarily along grain boundaries and at grain boundary intersections. The pores appeared to coalesce as reheat progressed. The growth rate was more rapid with a slope of 2/5. At $1300^{\circ}C$ the growth rate was more rapid than that for porous MgO but not as high as transparent MgO.

The fluorine samples (See Fig. 7) showed a cubic growth law both at $1500^{\circ}C$ and $1300^{\circ}C$. The grain sizes for a 1-hour reheat time can be compared with that obtained by Rice (Ref. 6) for a 2 wt% LiF addition. This as-pressed sample contained 0.9 at% F while our typical analysis gave a value of 0.52 at% F. At $1300^{\circ}C$ this work gave a value of 16μ for 1 hour,

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which was close to that of Rice (Ref. 6). At 1500°C for the same time our work gave a grain size of 30μcompared to a value of 40μ obtained by Rice.

The specimen (sample 74) initially doped with 3 at % OD did not show any retained OD after analysis but had 2.2 at% OH after hot pressing. The grain growth kinetics (See Fig. 10) showed again a cubic law at 1500°C and, because the chemical analysis shows OH, this specimen must be considered as OH doped.

The analysis and comparison of these data are continuing and further chemical analyses are being conducted on the reheated specimens to determine final anion concentration.

SECTION 3

DIFFUSION

The study of grain boundary diffusion of cations in the presence of anion doped material was planned to employ analysis of the cation distribution by means of neutron activation analysis. As specific samples were being prepared, it became apparent that difficulty in producing large samples of anion doped material would preclude the availability of sufficiently large samples for this technique. Subsequently, consideration was given to the technique of Zaplatynsky(Ref. 7) which uses color changes in MgO resulting from cobalt or nickel. However, it was found that this technique was not suitable when applied to polycrystal samples; firstly, because of the difficulty in obtaining specimens in which the grain boundaries were essentially perpendicular to the specimen surface, and secondly, color changes were not sharp.

Subsequently, arrangements have been made to use an electron beam microprobe. It is planned to produce specimens having uniform concentrations of nickel (obtained by means of a very fine grain size) for standards to be used to determine minimum detection limits at various probe settings. These settings will then be used to determine the spacial distribution of nickel at these various levels after diffusion anneals. Some samples have been prepared but no analysis results have been obtained.

SECTION 4

MICROHARDNESS

As has been stated previously, microhardness indentation was selected as a preliminary method of studying mechanical behavior because a number of different effects may be evaluated on small samples. The effects which can be considered are: 1) indent size, 2) indent dislocation wing length, and 3) fracture direction at higher indent loads. Use is being made of the first two effects in this research. The third has been excluded because it requires independent determination of the crystallographic directions in the polycrystals, a tedious though plausible study. Studies may also be made in which the crystallite size is small compared to the indent size and in which the indent size is small compared to the crystallite size.

Experiments have been conducted to define the experimental conditions, indent load and spacing. Figure 13 shows the data obtained. These results give the expected square root dependence of indent size on indent load. The apparent increase in hardness as a result of reduction of indent spacing suggests indent interaction. Additional studies including variations in surface condition are shown in Figure 14 and reveal the sensitivity of indent response.

First, surface hardness is critically dependent upon the means of preparation. Cleaved surfaces, for example, are considerably softer than those which have been mechanically polished; however, other workers (Ref. 8) have shown that these cleaved surfaces are not dislocation-free. However, the process of mechanical polishing produces considerable work and results in substantial further hardening. In addition, the extent of this hardening is not reproducible (compare polished and repeat in Figure 14). Studies are being conducted to ascertain whether reproducible results may be obtained by more precise control of the polishing procedure.

Secondly, the indents themselves introduce a zone of hardness surrounding the indent. Here the results suggest that approximately 75 to 100 microns between indents are necessary to reduce the interaction hardening to an amount less than that in the as-received crystal. Figure 13 suggests this zone to be independent of the applied load, a somewhat surprising conclusion since higher loads would be expected to produce larger zones of plastic deformation.

Thirdly, indentations in surfaces which had been cleaved under and indented under dry toluene exhibit increased indent size but not wing size. The increased hardness as evidenced by the indent size is consistent with the work of Westbrook(Ref. 9). However, the unchanged length of dislocation wings is unexplained. Westwood(Ref. 10) reports that time dependent glide of dislocation wings increases with the polarity of the solvent, and consequently wing size of indents made under ambient moisture would be expected to be larger for two reasons, greater indent size plus additional glide. An additional effect with measurements under dry toluene is reduced data scatter. Consequently, additional work here is being made under these conditions. The purpose here is to reduce scatter and not to specifically study atmospheric effects on dislocation glide.

It may also be seen in Figure 14 that the hardening introduced through the mechanical process may be reduced by annealing of the crystal. In the microhardness studies of specimens prepared by mechanical polishing, annealing to permit recovery of the crystals and subsequent microhardness study under toluene should provide better precision and sensitivity. It should be noted that minimum recovery conditions are necessary to prevent deterioration of the crystal surface during recovery and to prevent loss of the anion impurities due to diffusion. Consequently, more precise data on recovery would assist selection. Such work is underway.

In spite of these expected revisions of the procedure for obtaining grain boundary microhardness on the polycrystals, some data have been

obtained by means of conventional polishing and measurements in air. The details of the specimens are given in Table 3 and the hardness data across selected boundaries in Figs. 15, 16, 17 and 18. In these specimens there is no alignment of indenture with particular crystallographic orientation. Consequently, only changes as the boundary is approached are considered significant, and variation from crystal to crystal, specimen to specimen and scan to scan are not relevant because of possible variations in crystal orientation, local work hardening and bulk crystal composition.

These large grain specimens, where the indent size is considerably smaller than the grain size, again suggest the behavior of sulfur and chloride to be similar. No evidence of any grain boundary hardening was noted in Figs. 16 and 17. The data simply represent a scatter about an average value. It is hoped that this scatter will be reduced when the new techniques are employed. With the fluorine doped specimen some hardening at the boundary was noted and it is proposed that the ability of fluorine to substitute for oxygen on a size basis in magnesium oxide may cause some solid solution hardening.

Microhardness studies of fine grain specimens in which the indent size is larger than individual crystallites have been conducted and results are reported in Table 4. The data here represent only indent size, as dislocation wing length sizes are not determinable and would have no meaning in these fine grained specimens. Again data suggest a difference in behavior for the sulfur and chlorine doped specimens. In both of these materials the indents were badly fractured and, further, were larger, indicating a softer material. The expectation is that fluorine and OH substitute for oxygen and MgO may contribute to the increased hardness exhibited by specimens containing these impurities.

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SECTION 5

CHEMICAL ANALYSIS

The analytical studies of these anion-doped magnesium oxide materials are needed to provide information concerning the amount of these impurities remaining in the specimens during the various processing stages. The analytical procedures for these anions in ceramics are still subject to some question, especially those for hydroxyl. The results for sulfur, chlorine and fluorine use available procedures and are reported in the first annual report (Ref. 1). The chemical analysis of OH and OD in a solid oxide such as MgO has presented substantial difficulties to the analyst. Previous studies (Ref. 11) resulted in the development of an analytical procedure employing extraction of the OH impurities by oxygen at 500°C and subsequent mass spectrographic analysis. The extraction would require atomic mobility through the solid magnesium oxide grains at 500°C and thus suggests motion of individual hydrogen ions, since movement of a large hydroxyl ion, even along a chain of cation defects, seems unlikely at this temperature. This analytical procedure appears satisfactory for hydroxyl, although complete confirmation has never been obtained because of lack of suitable standards. However, it had never been employed in the analysis of OD but is being used here as the only available technique.

The typical range of results that have been obtained for these anion impurities is shown in Table 5. Note that there is a substantial loss of all volatile impurities during fabrication and subsequent heat treatment. The lower values are obtained with high temperatures and small specimens. Although the exact amounts of impurity vary slightly from specimen to specimen, these results may be considered typical of this work.

In general, the results for sulfur and chlorine show large reductions in concentration when the mechanical mixtures of powders are prepared into dense specimen and further reduced upon reheat. In contrast, the fluorine and hydroxyl exhibit significant anion levels upon fabrication but lose substantially on reheat. However, it should be emphasized that the reduction

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in grain boundary area during reheat is approximately two orders of magnitude, so if these impurities are largely associated with grain boundaries, the change in impurity atom per unit area of grain boundary does not decrease.

The analytical results for deuterium in MgO have been the source of considerable frustration and require considerable discussion.

Initially, specimens doped with 3 at% OD (KA75) and 3 at% OH (KA74) were prepared and pieces subsequently reheated to 900 °C and 1300 °C to enhance equilibrium conditions. The results of the analysis are shown in Table 6, and it may be seen that although OD was introduced into KA75 as the impurity anion, only hydroxyl (in the form of water, the equilibrium vapor specie) was observed. The amount of hydroxyl, although less than that present in the hydroxyl doped material, suggested that complete exchange between D_2O and H_2O had occurred during the preparation and mixing of the anion doped powders. The source materials were checked for D_2O concentrations, Table 7, and it was found that some exchange had occurred, but that the initial deuterated Brucite formed by the hydrolysis of MgO with D_2O still contained substantial deuterium. Subsequently, another hot pressing (KA87) was prepared entirely from deuterated Brucite. The material was loaded into the hot pressing die in a dry box and was pressed in an atmosphere of argon bubbled through D_2O at 25 °C. This specimen was subsequently analyzed (Table 8) by the extraction mass technique and again results showed insignificant deuterium levels. At this time the same specimens were then reanalyzed using spark source mass spectroscopy (no extraction), and the high ratio of OH to OD in this material was confirmed, although no absolute comparisons are available because of a lack of standards. The present conclusion of this experimental work is that deuterium exchanges with hydrogen occurs very rapidly in the Brucite and that all sources of hydroxyl must be eliminated. In the fabrication procedure used for KA87, the only possible source of hydroxyl is the

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refractory material within the hot pressing furnace. Some additional attempts are being considered to prevent this exchange. However, to date no specimens have been prepared in which chemical analysis has revealed significant OD and, consequently, no studies of other properties can be reported for OD doped material.

SECTION 6

FRACTURE STUDIES

These studies of the behavior of anions in a ceramic material were designed to assist in the evaluation of effects on both the general properties and, specifically, the mechanical behavior of ceramics. The phase of the work directed toward actual fracture studies is now beginning and experimental conditions, materials, etc., are being defined. Although it would be desirable to make studies entirely employing the anion-doped materials produced here, difficulty in determining the exact location of these anions (solid solution, second phase solid, entrapped gas) suggests the use of the material in which the microstructure can be more well defined. One such system which is closely akin to the materials studied here is iron-doped magnesium oxide. The microstructure of the material may be controlled by controlling the oxidation of the iron and the time during which the precipitates are permitted to grow. Such materials have been quite well defined by other workers and would appear to be useful here. Consequently, some preliminary studies are being made involving the hot pressing of iron-doped magnesium oxide and it is anticipated that these materials will be used in conjunction with anion-doped specimens during the fracture work.

SECTION 7

SUMMARY

The purpose here is to consider the results obtained throughout the various sections of this research to ascertain the general conclusions that one may draw. The foremost conclusion would be the quite limited solubility of chlorine and sulfur in magnesium oxide. This lack of solubility is supported by numerous factors. Firstly, chemical analysis reveals the failure to retain these impurities during fabrication and secondly, their serious interference with the densification during hot pressing. This further suggests that the impurities are rejected as volatile gases, although solid precipitates cannot be unequivocally ruled out at this time. Further, in the microhardness work, fine grained oxides containing these impurities exhibit grains which are easily broken out by a microhardness indenture. This again could be the result of small pores containing a trapped gas phase. Finally, the scans of hardness across grain boundaries show no effect of these impurities, probably resulting from their low concentrations and their residence in pores which would have little influence on individual grain boundary mechanical behavior.

These statements may be almost completely reversed in the case of fluorine and to some extent for hydroxyl. Levels of these anions after reheating remain moderately large (approximately 1-2 at%). Further, the effect on fabrication is much less and grain growth appears to be either unaffected or improved. Further, the room temperature microhardness of the fine grained material is little changed either quantitatively or qualitatively; however, indications of grain boundary hardening are observed, suggesting segregation of the soluble fluorine to the grain boundaries.

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Table 1

Physical Properties of Anion Impurities

Specie	Diameter		Vapor Pressure @ 1000°C (atm)[†]	
	$\overset{\circ}{A}$	% difference from $O^=$	Element	$Mg\ X_n$
$O^=$	2.80	0	$> 10^3$	$< 10^{-6}$
OH^-	2.76	-1.4	$\sim 10^3$	15
OD^-	2.76	-1.4	$\sim 10^3$	15
F^-	2.72	-2.9	$\gtrsim 10^4$	$< 10^{-6}$
Cl^-	3.62	+29.2	$> 10^3$	0.03
$S^=$ *	3.68	+31.4	15	$< 10^{-6}$

[†]Data from Handbook of Physics and Chemistry
and use of Duhring's Rule when necessary.

* The formation of SO_2 or SO_3 would result in a
high vapor pressure and would suggest all
anions to have comparable deleterious effects.

Table 2

Characteristics of Specimens Used in Grain Growth Studies

Specimen No.	Dopant At% Kind	Hot-Pressing Conditions Pressing Temp. (°C)	Atmosphere	As-pressed Density gm/cc	As-pressed Analysis At% Kind
30	0.6 S	955	Vacuum	3.507	0.025 S
33	0.6 S	960	Vacuum	3.426	N.A.
96	3 S	1100°	Vacuum	3.489	N.A.
48	3 Cl	1170°	Vacuum	3.422	N.A.
110	3 F	1100°	Vacuum	3.529	N.A.
112	3 F	1100°	Vacuum	3.518	1.088 F
74	56 OD	1050°	Argon	3.411	2.2 OH*

N.A.   - not available for this particular specimen,
see Table 5 for typical analysis.

* Specimen initially doped with OD but not found in
the analysis.

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Table 3

Anion Doped MgO Polycrystals Used For
Grain Boundary Hardening Studies

Specimen Number	Anion Dopant[1]	Reheat Conditions	Density (gm/cm^3)
30	0.03 at % S	110 hr. @ 1500°C	3 42
47	.1 at % Cl	48 hr. @ 1500°C	3.42
65	0.93 at % F	120 hr. @ 1500°C	3.37
74	2.2 at % OH[2]	75 hr. @ 1450°C	3.41

[1] Typical analysis of as pressed specimen - Reheat analysis not available but typically .01 - .05 at %.

[2] Specimen initially doped with OD but not found in analysis.

Table 4

Indentation Size for Hot Pressed MgO Containing Anion Dopants and Average Grain Size ≤ 1μ

Specimen #	Dopant at%	Average Indent Size(μ)	
40	.2%S	7.85±	indents fractured
76	1.7% OH	5.50± .35	
52	.1% Cl	~ 9	Indents badly fractured
58	1% F	6.41± .28	

Table 5

Concentrations of Anions (at%) in Hot-Pressed MgO

Specie	Powder	As Pressed $\sim 0.5\mu$ grain size	Reheat $\sim 100\mu$ grain size
Cl	3	.06 - .5	.01 - .05
S	3	.15 - .6	.01 - .05
F	3	.9 - 1.5	.02 - .05
OH	3[1]	1.7 - 2.3	.1 - 1.5
OD[2]	-	-	-

[1] Not including ~ 0.5 in as-received powder

[2] See text,

Table 6

Concentration of H_2O, HDO, D_2O (PPM by weight except wt % as noted) in MgO after extraction as noted.

	100°C Vac			500°C Vac			500°C O₂		
	H_2O	HDO	D_2O	H_2O	HDO	D_2O	H_2O	HDO	D_2O
KA 76 MgO + 3 at% OH									
as pressed	200	-	-	6400	-	-	2.3%	-	-
900°C RH	30	-	-	1800	-	-	2.3%	-	-
1300°C RH	6	-	-	20	-	-	2.2%	-	-
KA 75 MgO + 3% OD									
as pressed	30	-	÷	1300	23	-	1.7%	74	-
900°C RH	40	6	-	370	-	-	1.7%	-	-
1300°C RH	9	-	-	280	2	-	1.8%	-	4

Table 7

Anion Concentration from Decomposition of $Mg(OD, OH)_2$ by Mass Spectrographic Analysis as a Function of Decomposition Temperature and m/e Ratio.

m/e	Source	Intensity at various decomposition temp.				
		60°C	100°C	150°C	200°C	250°C
17	OH^+	4.90	1.14	1.31	1.64	1.04
18	OD^+, H_2O^+	16.38	4.72	4.40	5.40	0.97
19	HDO^+	7.32	2.61	4.16	5.33	4.66
20	D_2O^+	0.3	0.45	0.82	1.29	0.52

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Table 8

Analysis of MgO for OH, OD, and HDO

Sample	Compound	ppmw		
		100°C	500°C	500°C with O_2
KA No. 87 Reheat 1300 C	H_2O	4.	700.	6160
	D_2O	0.01	0.2	<0.04
	HDO	0.09	10.	25.
	OD	<0.1	<0.1	<0.4
	H_2	ND	93.	<0.01
	HD	ND	<0.01	<0.01
	D_2	ND	<0.01	<0.01
KA No. 87 as Pressed	H_2O	236.	1230.	19000.
	D_2O	0.3	1.	2.
	HDO	0.4	23.	17.
	OD(Max. possible)	<0.1	<0.1	34.
	H_2	ND	4.	<0.01
	HD	ND	0.8	<0.01
	D_2	ND	0.01	<0.01

ND - not determined
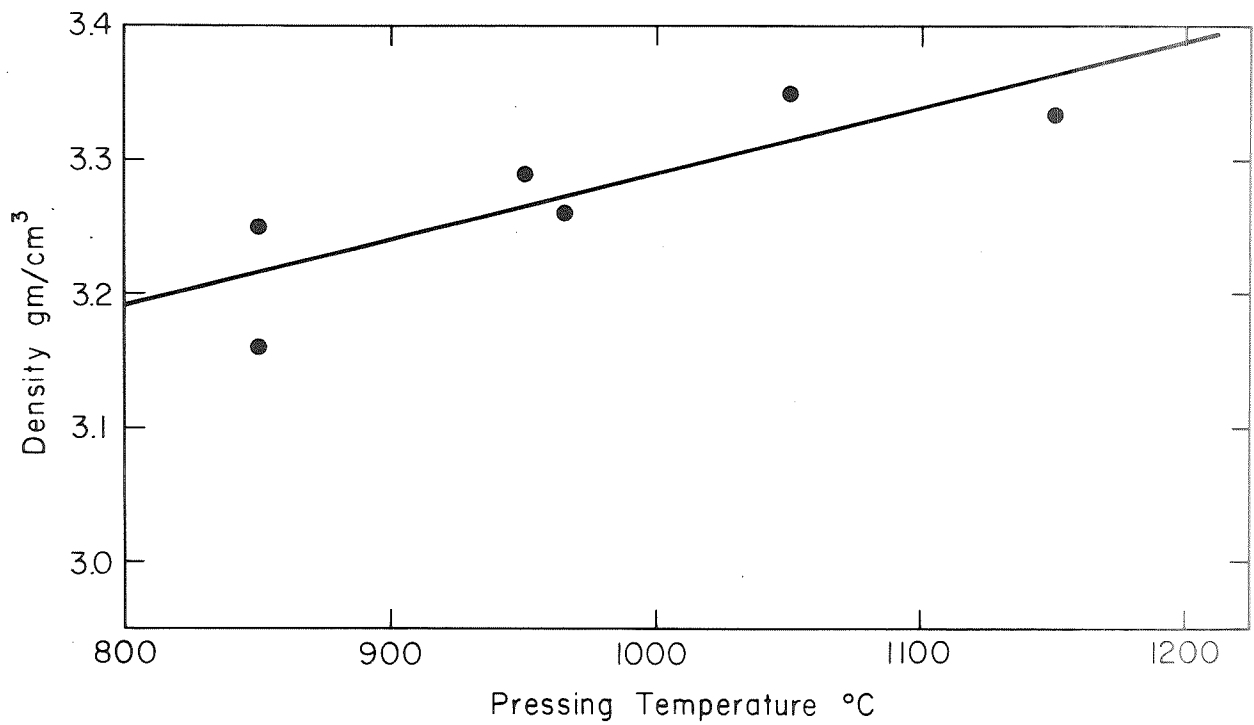
Fig. 1. Density versus hot pressing temperature for
Fisher M-300 MgO doped with F⁻

25
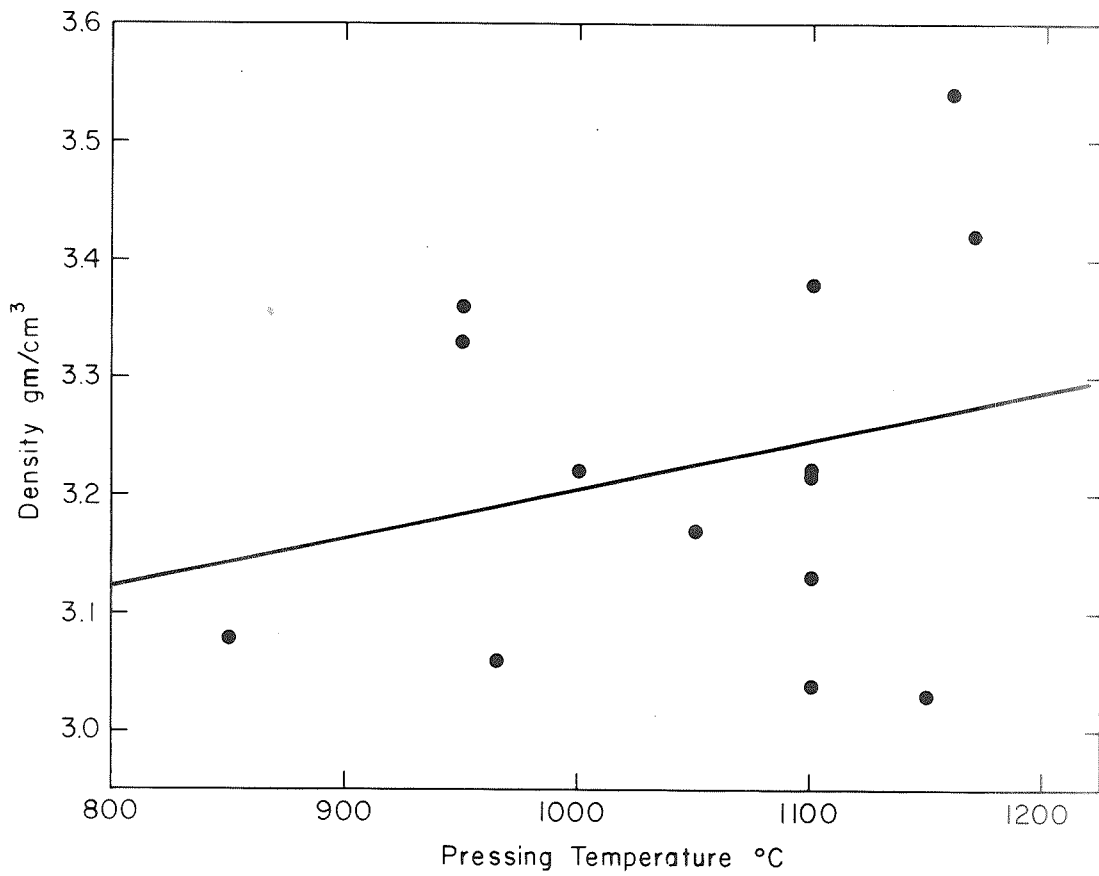
Fig. 2. Density versus hot pressing temperature for
Fisher M-300 MgO doped with Cl⁻.

26
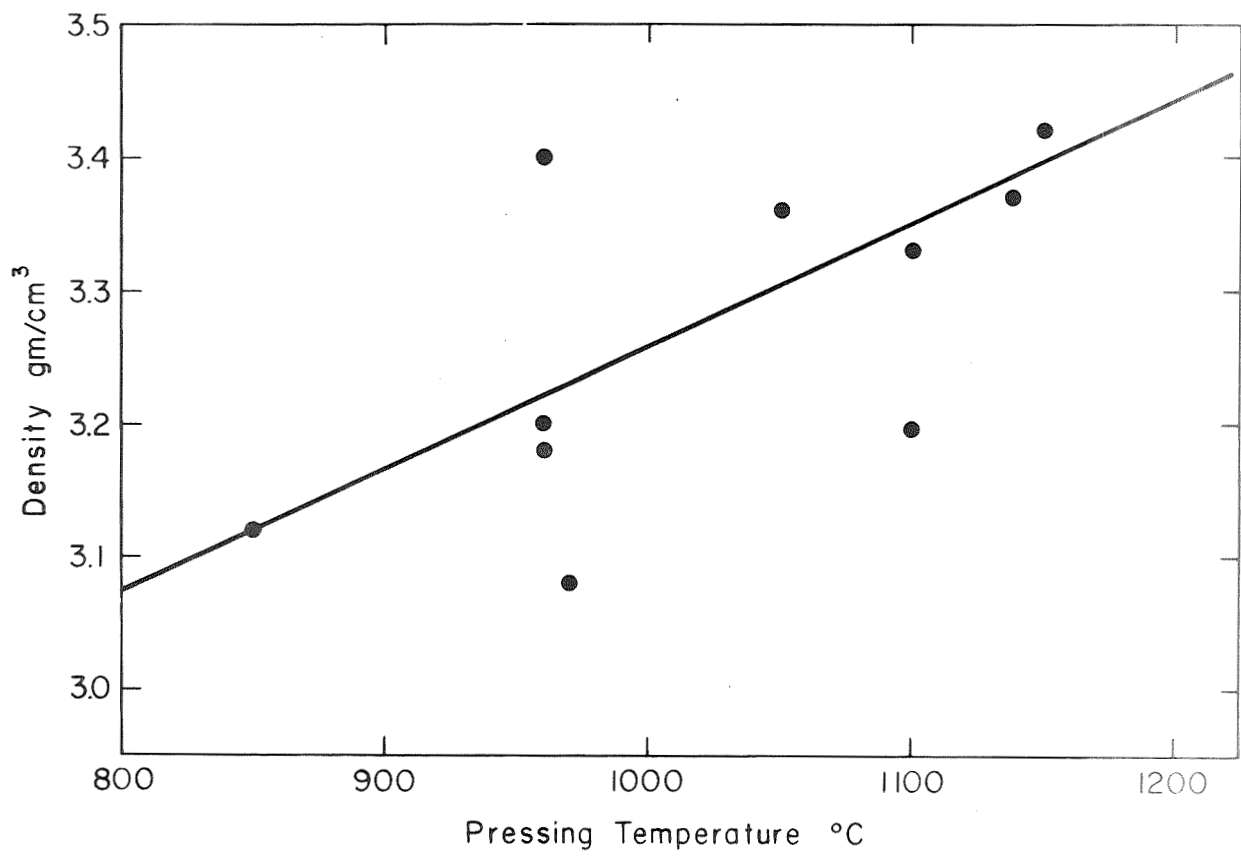
Fig. 3. Density versus hot pressing temperature for
Fisher M-300 MgO doped with S=.

27
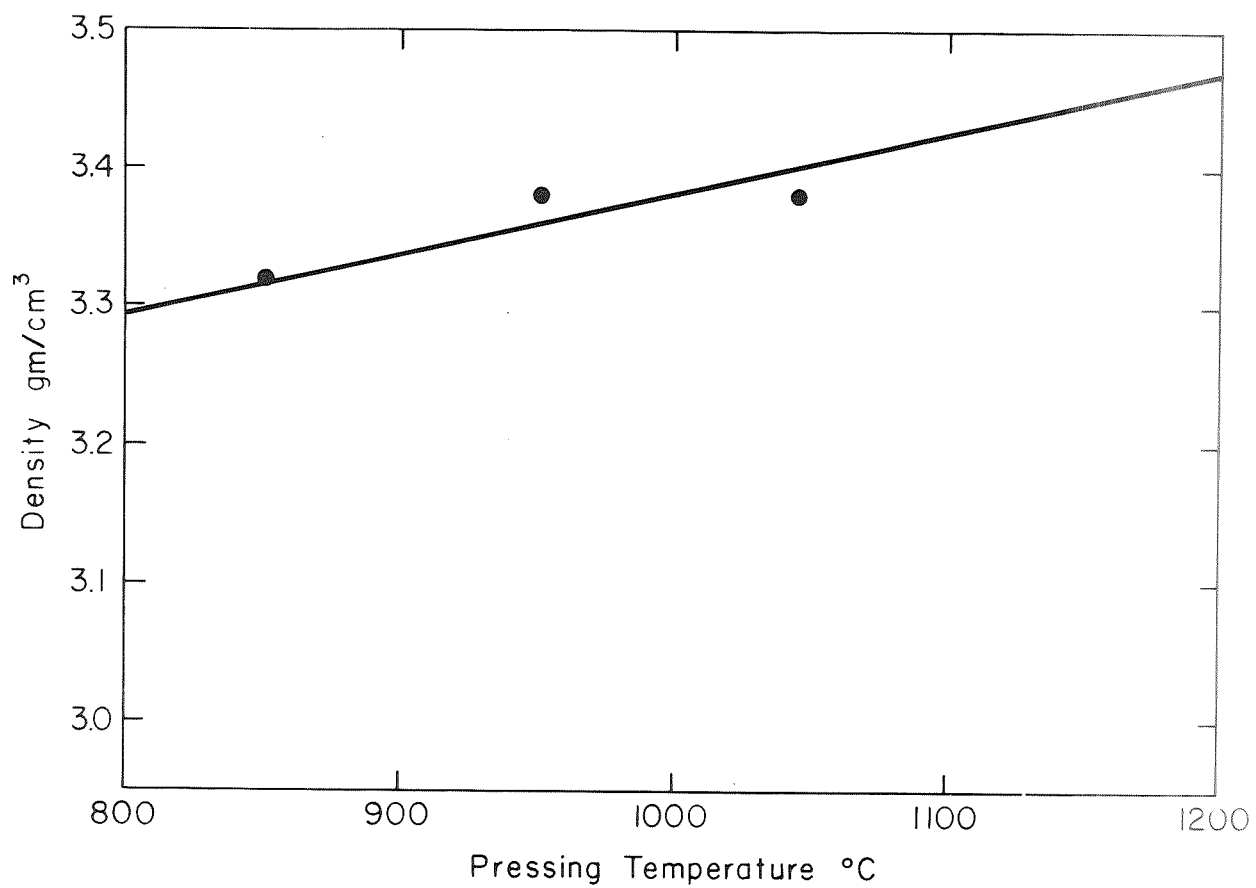
Fig. 4.   Density versus hot pressing temperature for
Fisher M-300 MgO doped with OH⁻.

28
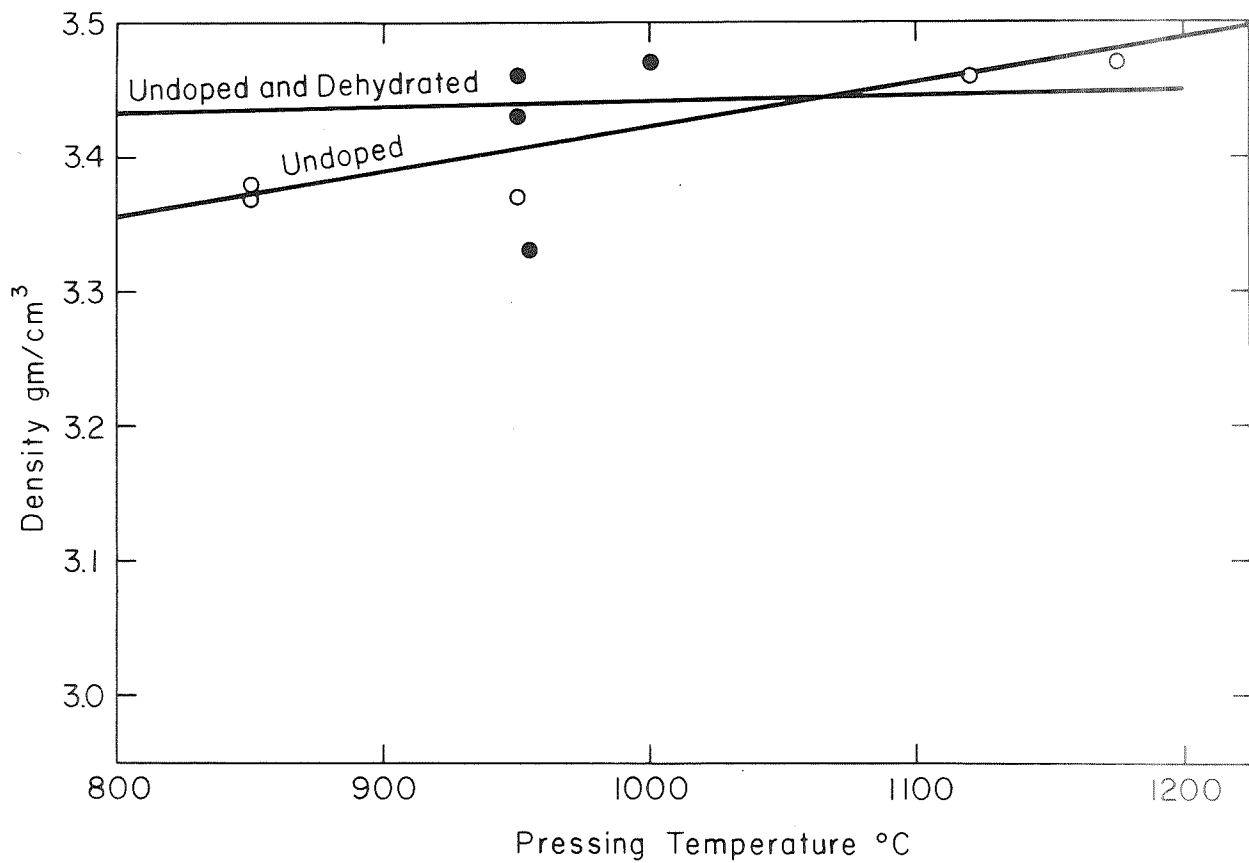
Fig. 5. Density versus hot, pressing temperature for
         Fisher M-300 MgO as received and dehydrated.

29
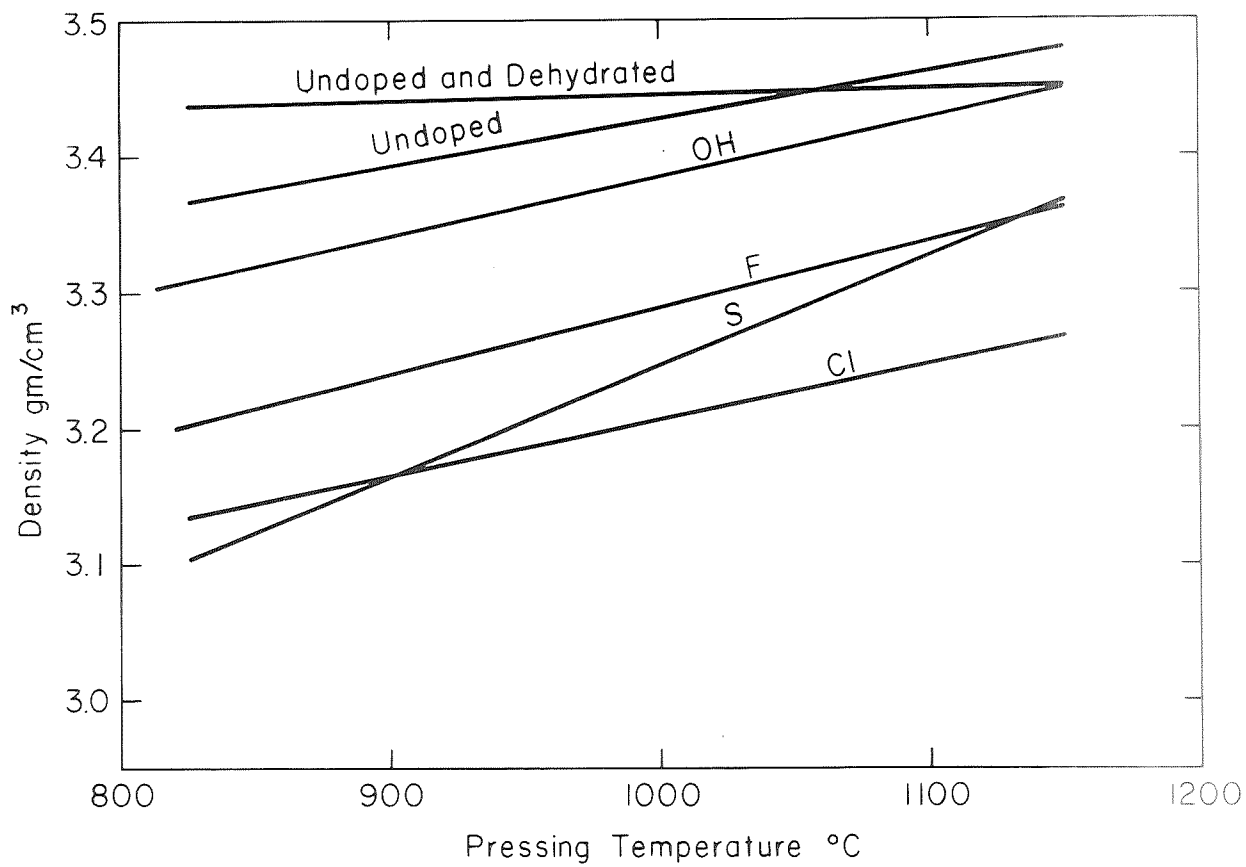
Fig. 6. Density versus hot pressing temperature for Fisher M-300 MgO with various anions.

30
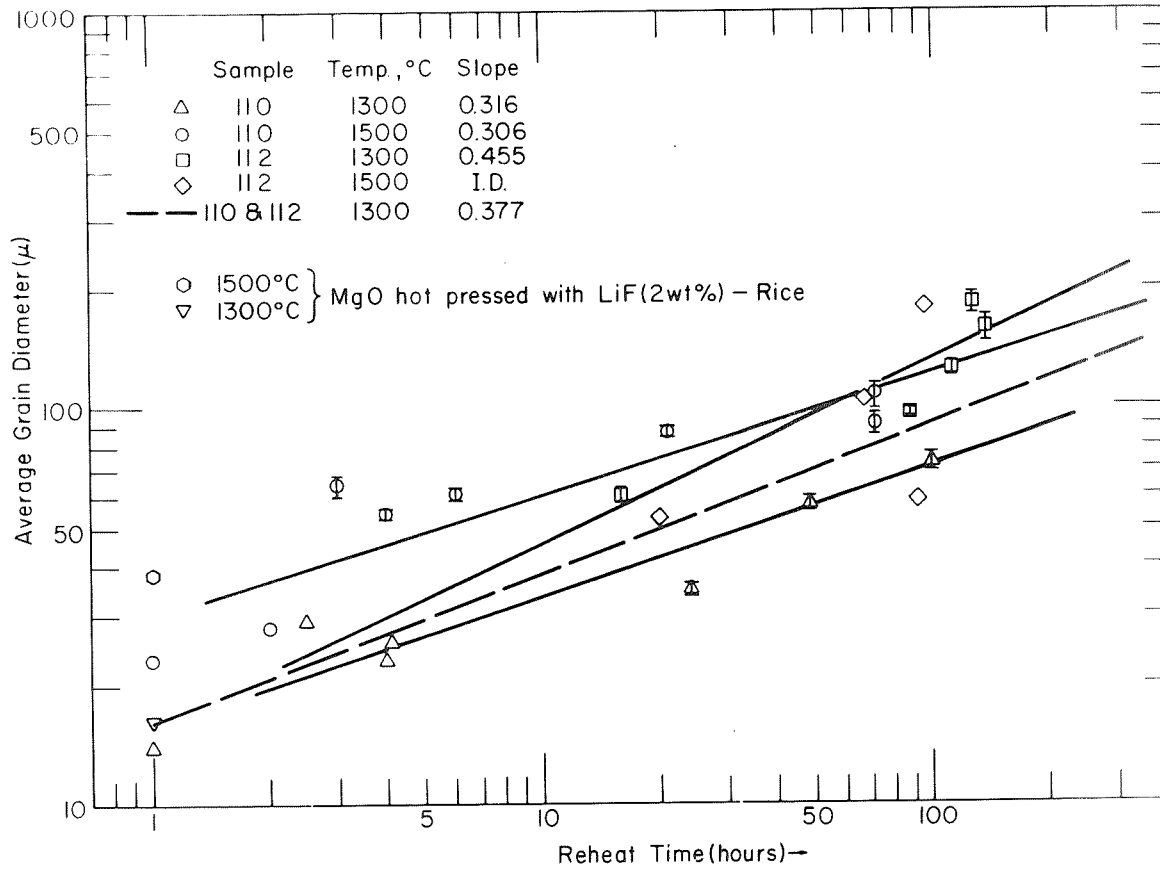
Fig. 7. Grain Growth in MgO doped with fluorine.

31
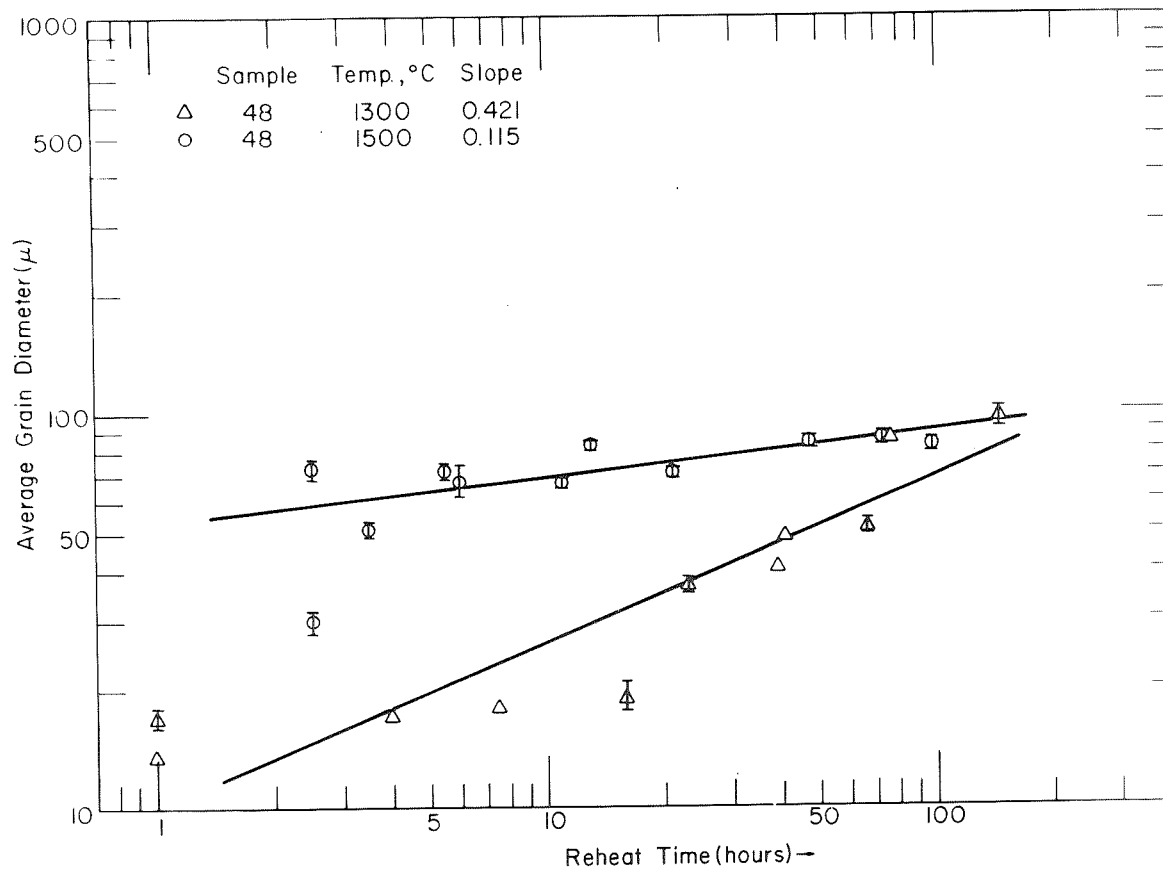
Fig. 8.   Grain Growth in MgO doped with chlorine.

32
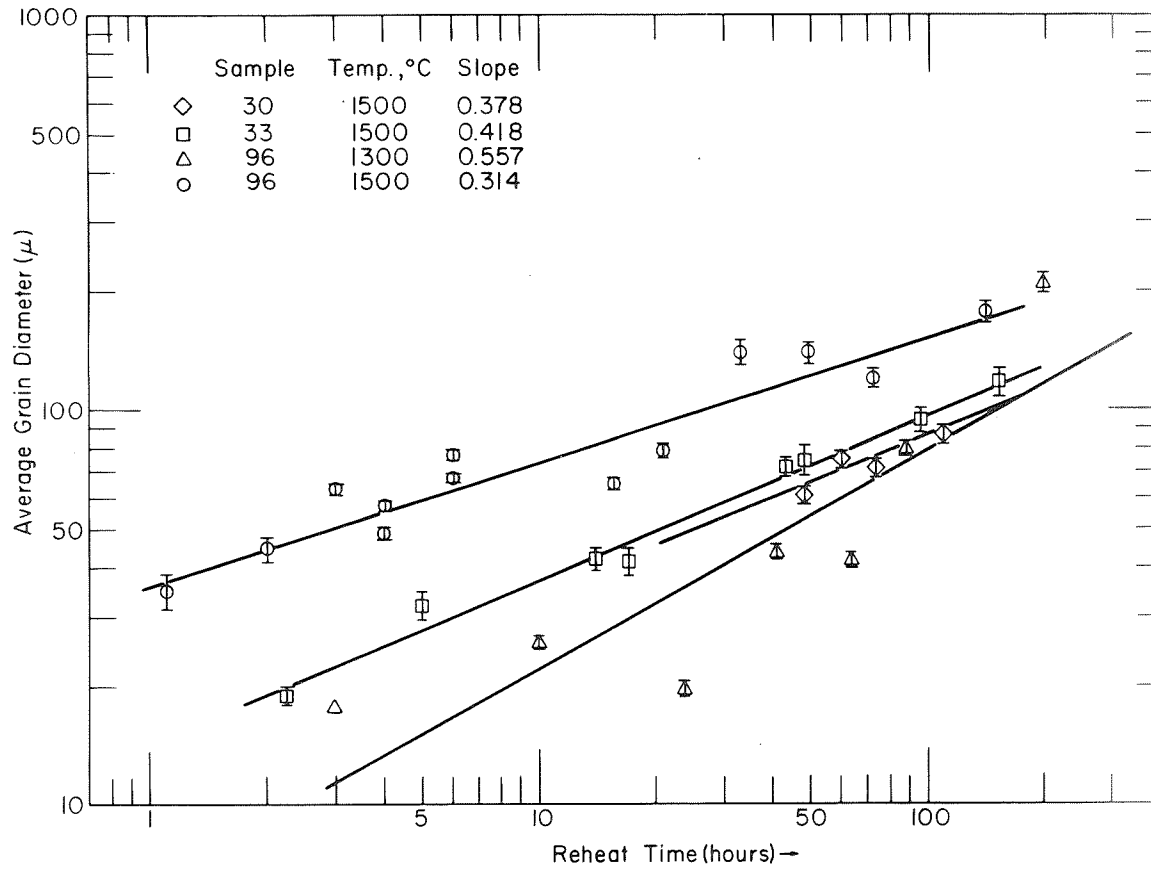
Fig. 9. Grain Growth in MgO doped with sulfur.
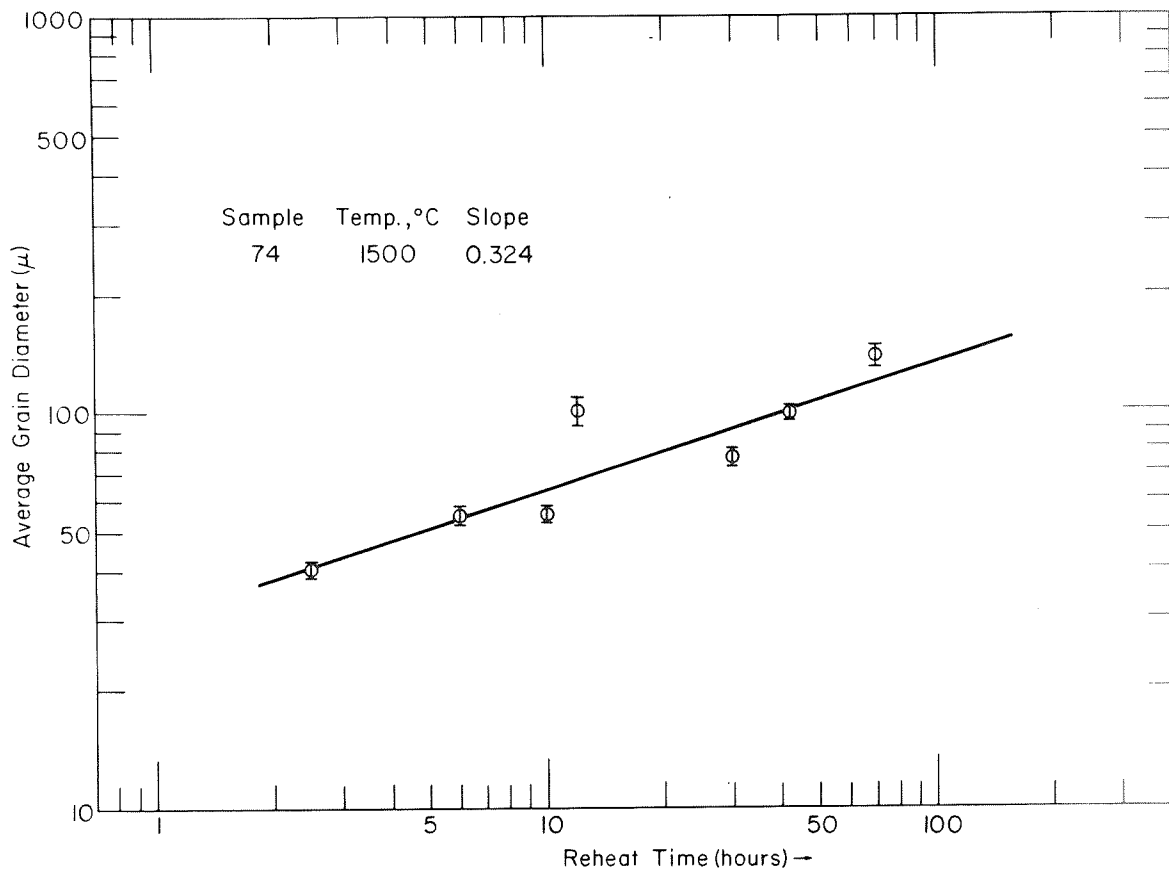
Fig. 10. Grain Growth in MgO doped with hydroxyl.
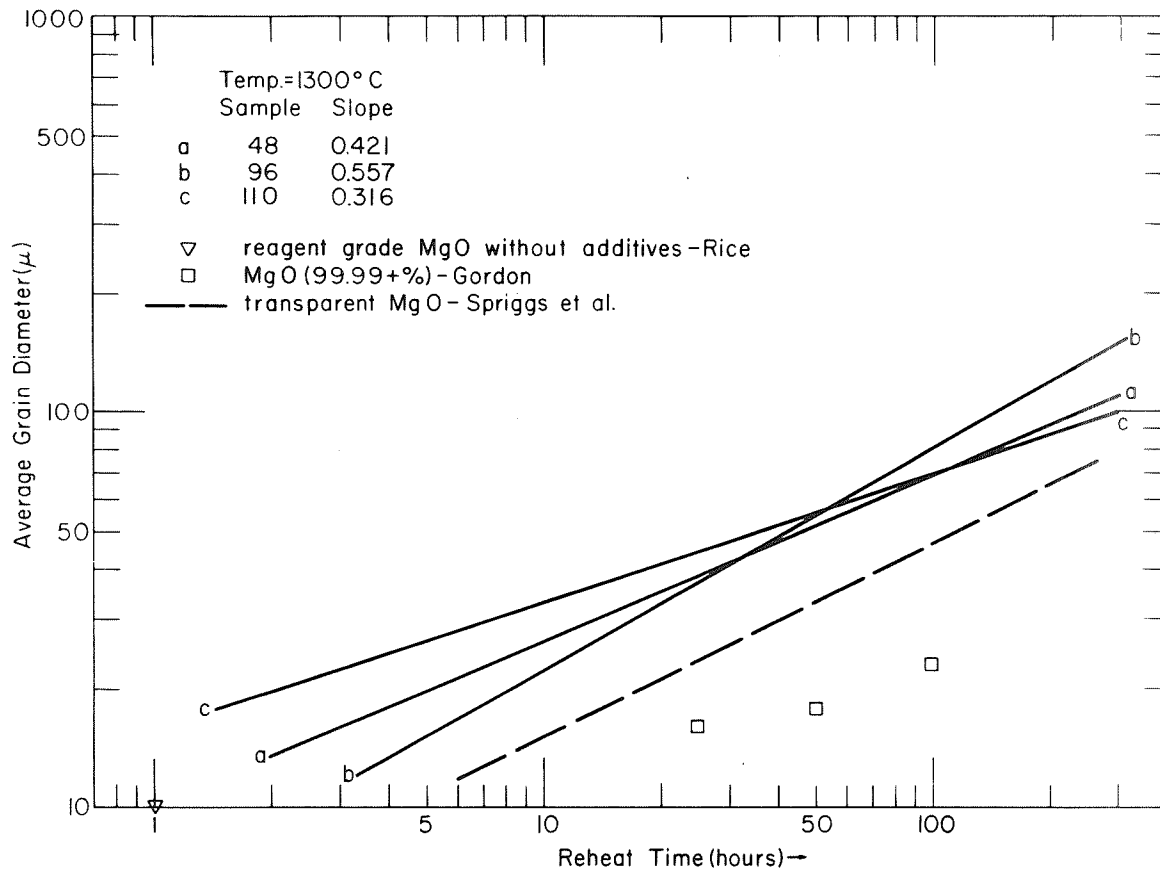
Fig. 11. Grain Growth in MgO at 1300 °C.

35
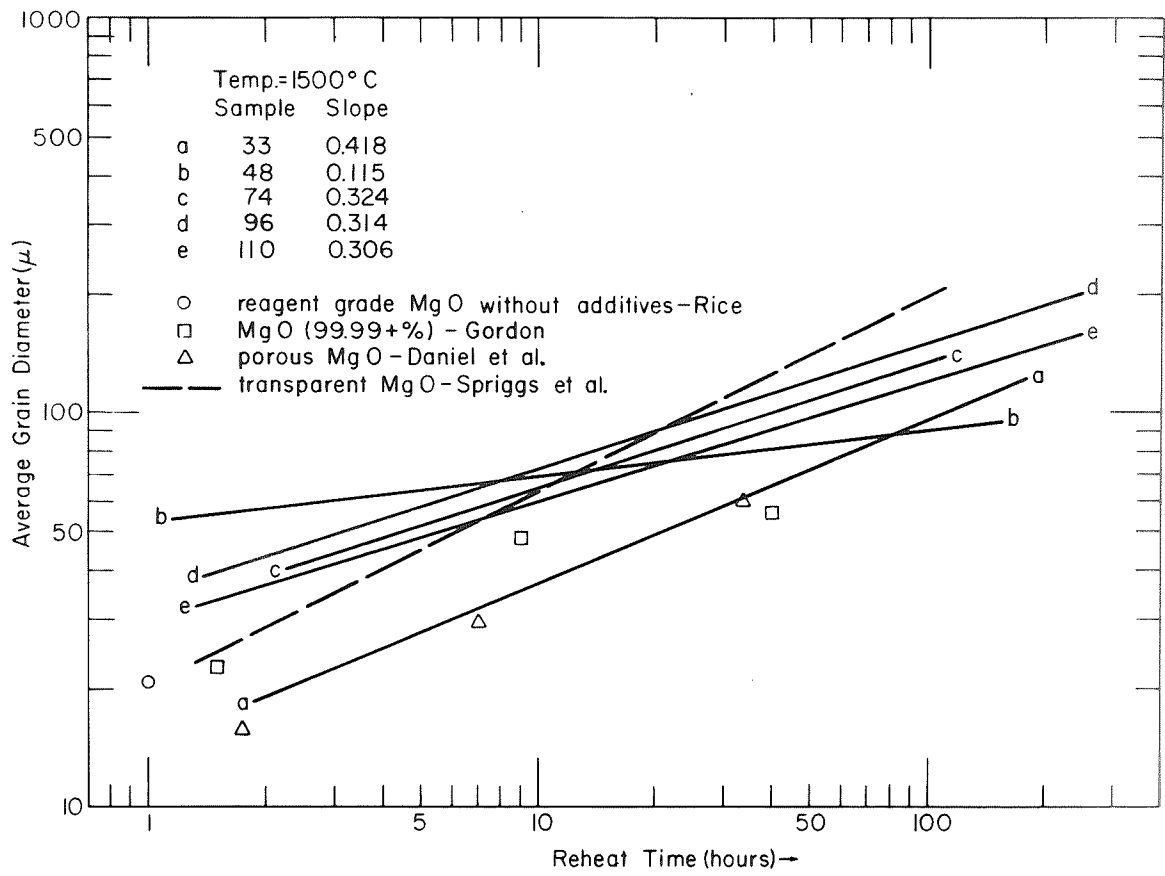
Fig. 12.   Grain Growth in MgO at 1500°C.

36
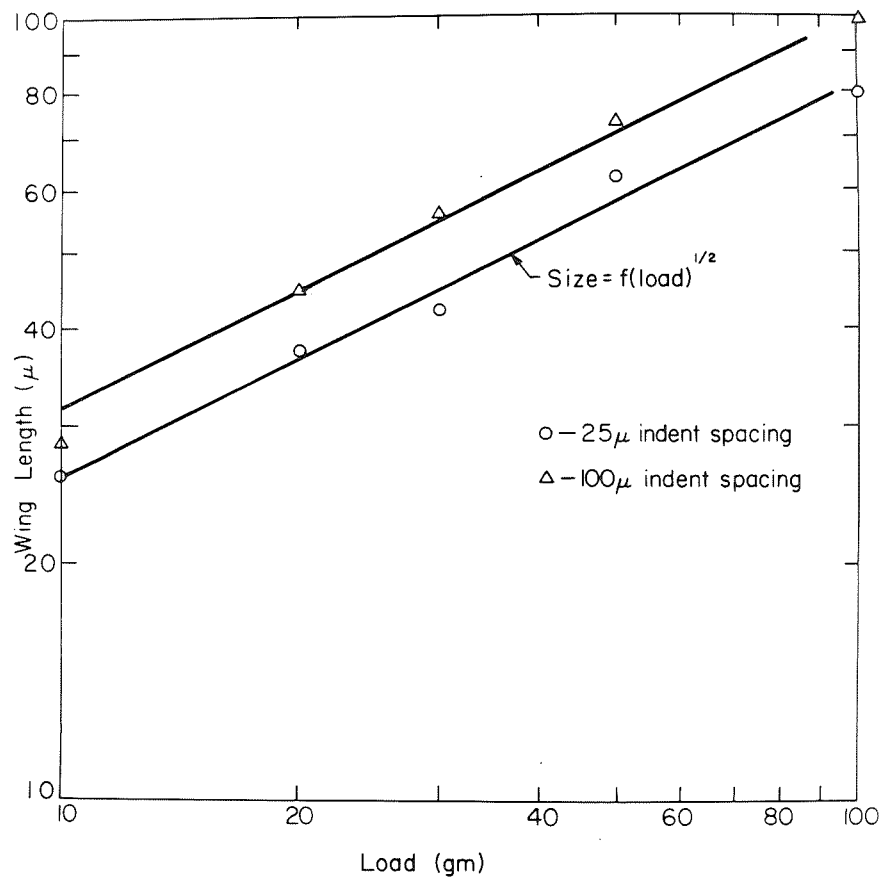
Fig. 13.   Wing size on cleaved (100) MgO surface as a function of indent load.   Line represents theoretically expected result.
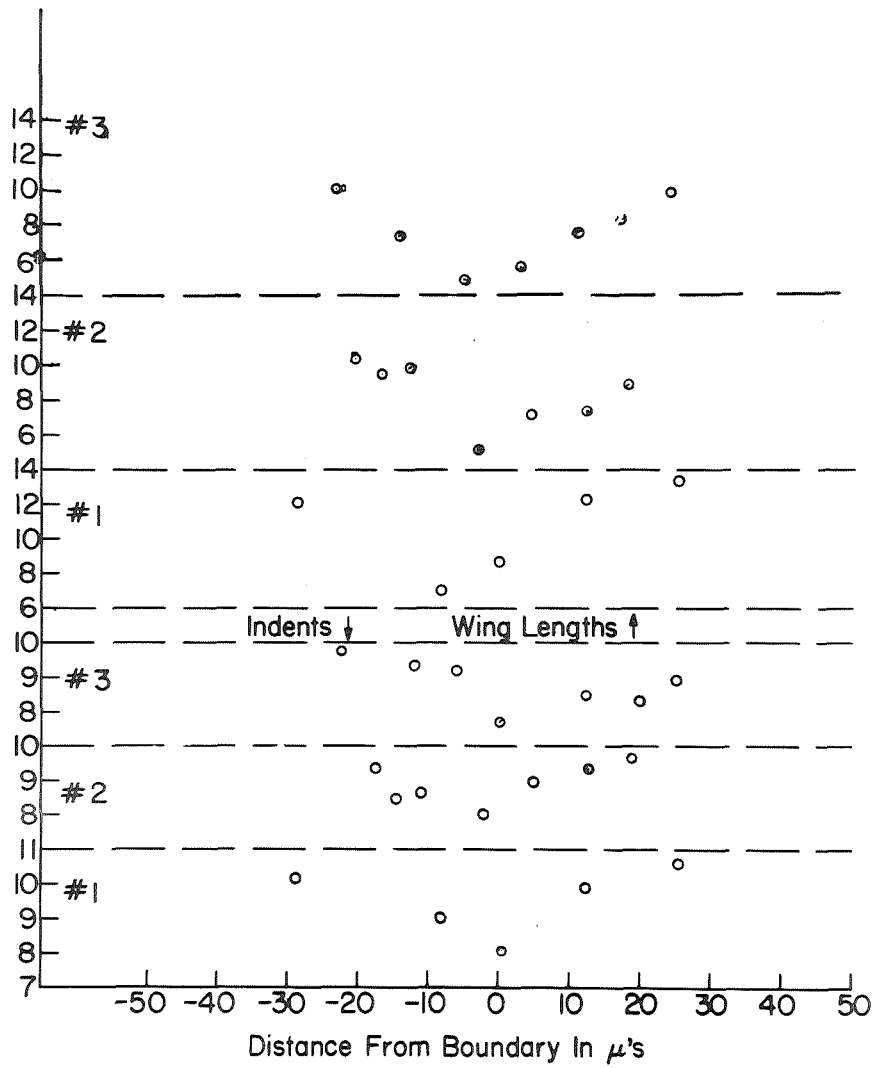
37

Fig. 14. Indent size versus wing size at 30 gram load for Norton single crystal MgO and various surface conditions.
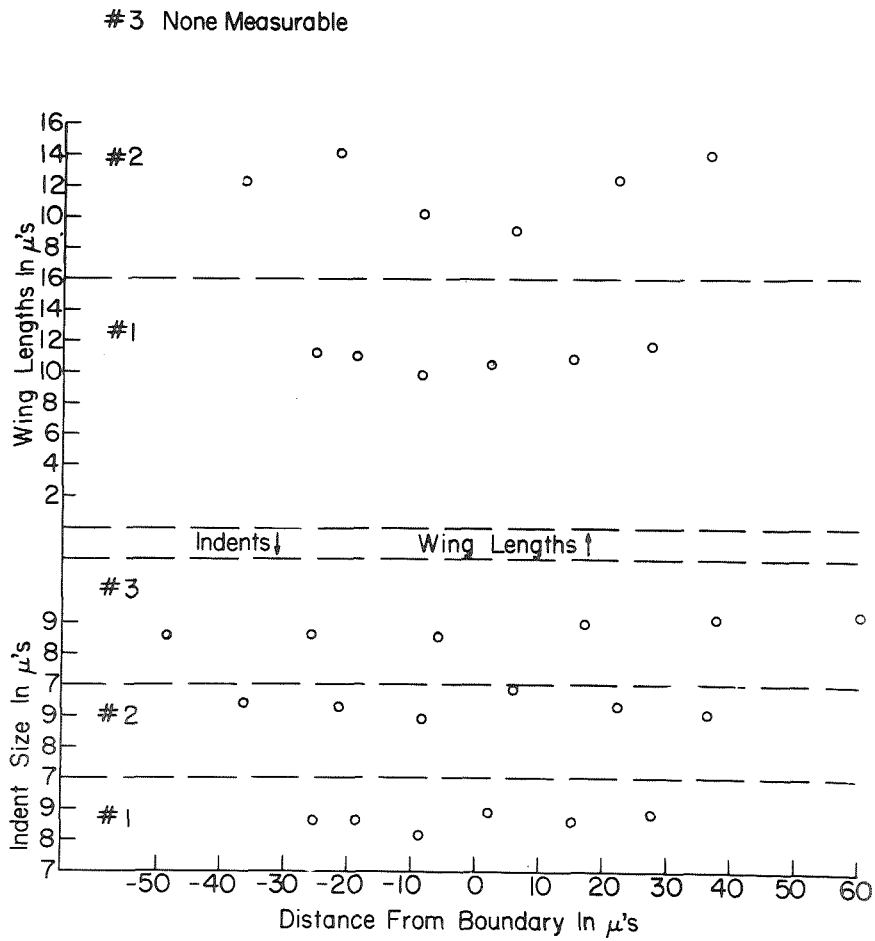
38

Fig. 15. Microhardness indent size and wing spacing scans across 3 boundaries in anion F doped MgO specimen #65.

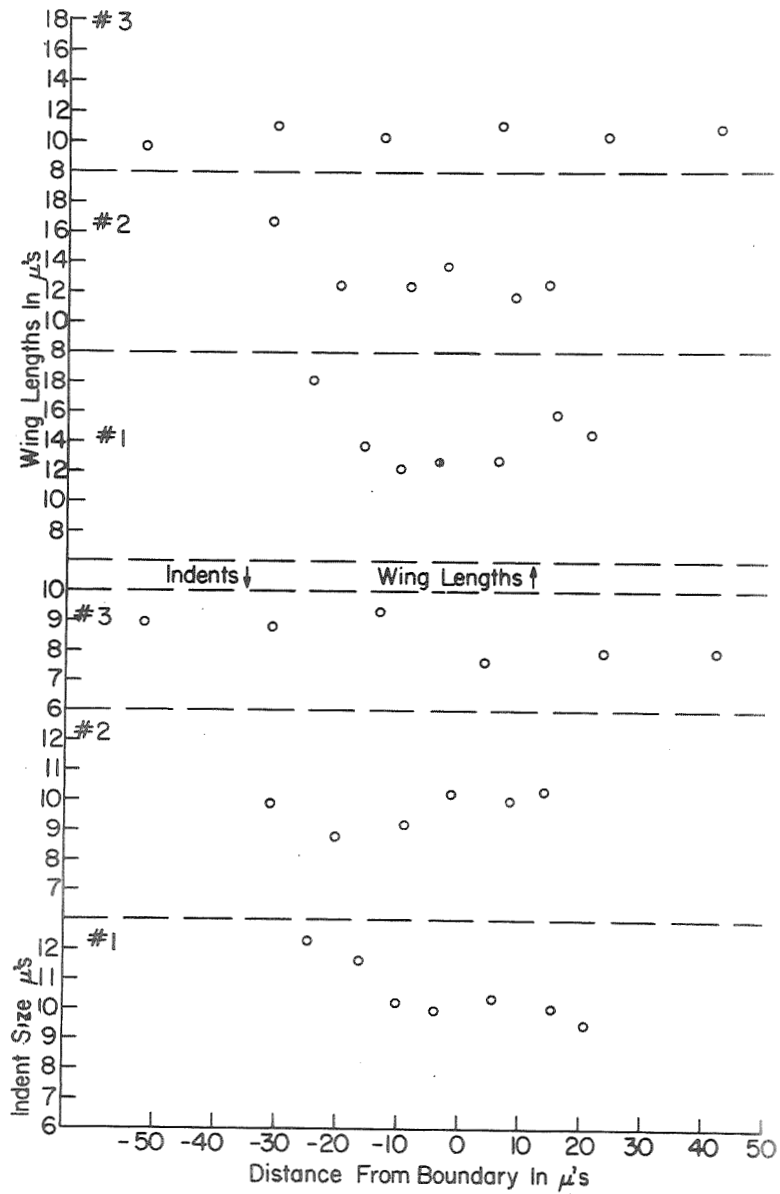Fig. 16. Microhardness indent size and wing spacing scans across 3 boundaries in anion Cl doped MgO specimen #47.

40

Fig. 17. Microhardness indent size and wing spacing scans across 3 boundaries in anion S doped MgO specimen #30.
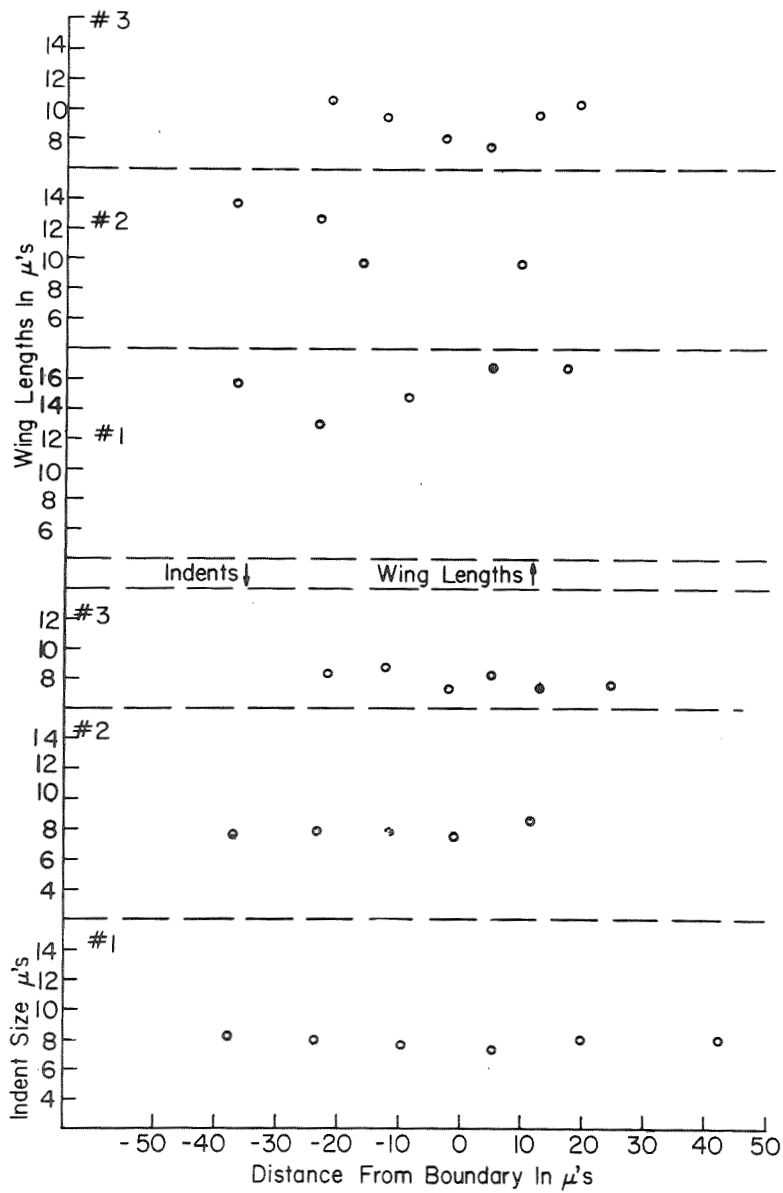
41

Fig. 18. Microhardness indent size and wing spacing scans across
3 boundaries in anion OH doped MgO specimen #74.

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