

# Segregation of calcium to magnesium oxide grain boundaries

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**Abstract.** Grain boundary (GB) segregation has been measured in Ca-doped MgO by examining intergranular fracture surfaces with Auger electron spectroscopy. The measurements reveal several interesting features. The composition of any given GB on the fracture surface is almost uniform, except for small variations due to deviations from planarity. There is a strong anisotropy of GB composition, which can amount to as much as a factor of six between low and high segregation GB's. Finally, although the compositions of opposite sides of a GB fracture are uniform, there are sometimes significant differences between the two sides, in agreement with a recently formulated model of GB composition as a function of GB character.

## Introduction

Calcium is known to segregate strongly to both MgO surfaces and grain boundaries (GBs) [1-4]. In the context of GB's, it has been shown that calcium segregation is anisotropic, i.e. it varies from one GB to another [3], and thus appears to depend on GB "character". Here we use the term character to mean the five macroscopically observable parameters that specify the lattice misorientation of a boundary and the orientation of the grain boundary plane and, therefore, determine both the structure and energy of a GB. In addition to these variables, there are also three microscopic degrees of freedom which may affect the GB structure and energy. For the purposes of this paper, we will assume that these additional parameters have achieved their equilibrium values at all boundaries, so that only the macroscopic parameters are needed to define the character of a GB. While our ultimate objective is to determine whether there exists a direct correlation between GB composition and character, the thrust of this paper is to establish certain characteristics of GB segregation which are prerequisite to reaching this ultimate goal.

To study grain boundary composition, we have investigated MgO polycrystals doped with Ca. We use the well-developed approach of fracturing specimens along GB's, and then analyzing the composition of the surfaces of the parted boundaries by Auger Electron Spectroscopy. This approach tends to yield reasonably quantitative determinations of the near-boundary composition.

The purpose of this paper is to attempt to answer the following two questions about the nature of GB segregation, within the context of the present experimental approach. First, is the composition of a given GB uniform across the whole interfacial area? The reason for posing this question is to test our assumption that a well-equilibrated boundary should have constant microscopic parameters over its entire area. Of course, the composition of a given boundary would be expected to vary over

its area if it were not perfectly planar, since the grain boundary character would then be different at different points. However, if the composition of a perfectly planar GB differs from one area to another, this would imply that the microscopic grain boundary parameters are not constant on a single well-equilibrated interface. The literature indicates that this may be the case. For example, some computer simulations of GB composition have occasionally revealed differences in composition and/or structure, from one simulation to the next, for boundaries with identical macroscopic parameters [5]. However, simulations tend to address very small GB areas (in comparison to the size of an analytical probe), and are subject to trapping in meta-stable states, a feature which may not be present in real materials. Experimental evidence in the literature on composition variability over a given GB is mixed. In studies of P segregation in Fe-P alloys, and of Bi segregation in Cu-Bi alloys, Rothman and Menyhard [6] found that the variability of segregant composition from point to point on any given GB fracture facet was essentially similar to the experimental error obtained at a given point. However, on faceted GB's, the segregant concentration varied significantly from one GB facet to another. Since different facets represent different GB inclinations, this result is not disturbing. In some measurements of radiation-induced GB segregation, Bruemmer et al. [7] showed measurable variations of Cr and Si at single GB's in stainless steels, although in this case also, the variability within a given boundary was smaller than the variations in composition observed among different boundaries. Such behavior could be due to several factors, including lack of planarity or incomplete equilibration. The latter possibility is particularly likely in complex systems with several segregating elements, each of which could display different segregation kinetics. We have therefore chosen a relatively simple system, with only one segregating species, to avoid complex inter-species interactions, which could conceivably cloud the issue.

The second question we wish to answer is, what can one expect to find if compositions are measured on the two halves of a fractured GB? This is an important question in the context of GB composition studies on fracture surfaces. Little is known about the path of an intergranular fracture at the atomic scale. Where does that path lie? Does it split the GB "down the middle", such that the fracture produces two fairly perfect surfaces with  $\{hkl\}$  indices corresponding to the crystal planes which terminate the two adjacent crystals? Or, does the fracture path zigzag slightly across the GB such that it samples the segregated regions on both sides of the boundary? In the first case, one might expect some differences in composition between the two halves of the boundary, since any differences in the indices of the terminating surfaces would be expected to influence at least the composition gradients of segregant of each half, and possibly the actual compositions of the terminating planes. In the second case, the compositions of the two sides would be expected to be quite similar, as long as the amplitude of the zigzag were small compared to size of the analyzed area. Some information on this subject has been obtained from GB fracture studies in alloys. In the case of P-doped Fe-Si alloy bicrystals [8], it was shown that the fracture path can indeed zig-zag from one side of the GB to the other, thereby splitting a symmetric boundary into two surfaces of patchy compositions. In the case of zig-zag fractures, the fracture path was deflected from one side of the boundary to the other by the presence of deformation bands. Such phenomena are less likely in the GB's of brittle materials such as MgO.

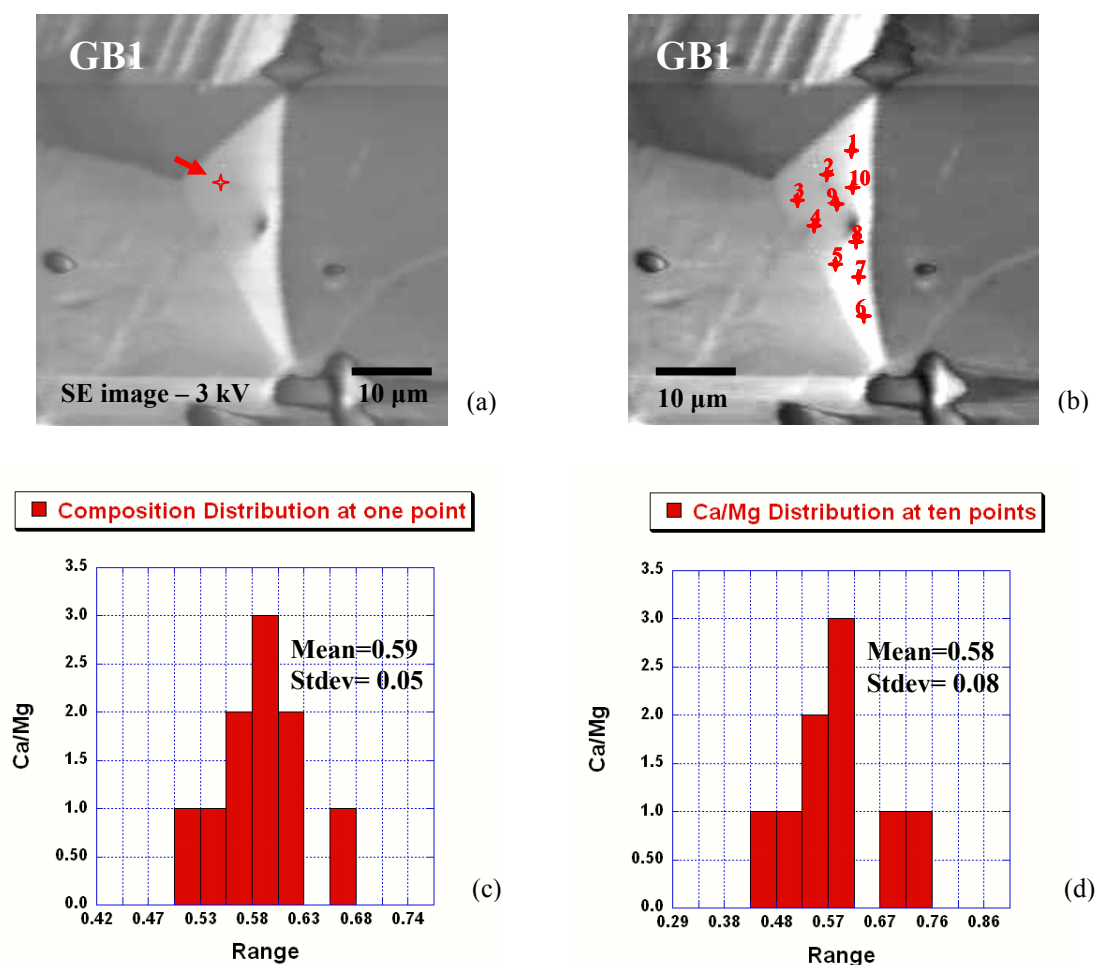
## **Experimental procedure**

The material used in this investigation was polycrystalline MgO doped with Ca at levels ranging from 1000 to 3000 ppm. Samples were prepared from MgO and CaO powders produced by calcination of the respective carbonates. The powders were ground together to ensure uniform solute distribution. After cold pressing, compacts were sintered at 1600°C for 15 hours, leading to a grain size ranging from 10 to 100µm.

Specimens were fractured in air in order to reveal internal interfaces. Immediately after fracture, both halves of the fractured specimens were introduced into the ultrahigh vacuum chamber of PHI Model 600 scanning Auger microprobe (SAM), for analysis of both matching sides of the GB fracture surfaces. Auger analyses were carried out at a pressure of  $\sim 2 \times 10^{-10}$  Torr, at 3keV, with a beam current of  $\sim 50$  nA and an analytical spot size of about  $1 \mu\text{m}$ . No significant charging effects were observed in these measurements. Indeed the energies of the O, Mg, and Ca Auger transitions were found at 511 keV, 1175 keV, and 291 keV, respectively. These values are consistent with the energies determined by Seah [9], in a study of charging effects on MgO single crystals by electron beams. Auger data were acquired in the derivative mode, and the peak-to-peak amplitudes were determined for each element. In this work, no reference standards were used, but the Ca/Mg ratio for each GB was determined, thus yielding a relative segregation level.

## Results and discussion

**Estimate of experimental scatter.** To determine the intrinsic experimental scatter in the Auger measurements, the composition was measured ten times at the same point. To determine the uniformity in the composition on a single boundary, the composition was measured at ten different locations. An example of these data is illustrated in Fig. 1.



**Fig. 1.** Secondary electron images showing the locations on GB1, where the experimental scatter has been measured (a) at one single point, (b) at ten different points, and histograms displaying the Ca/Mg distribution (c) at one point, (d) at multiple positions across GB1.

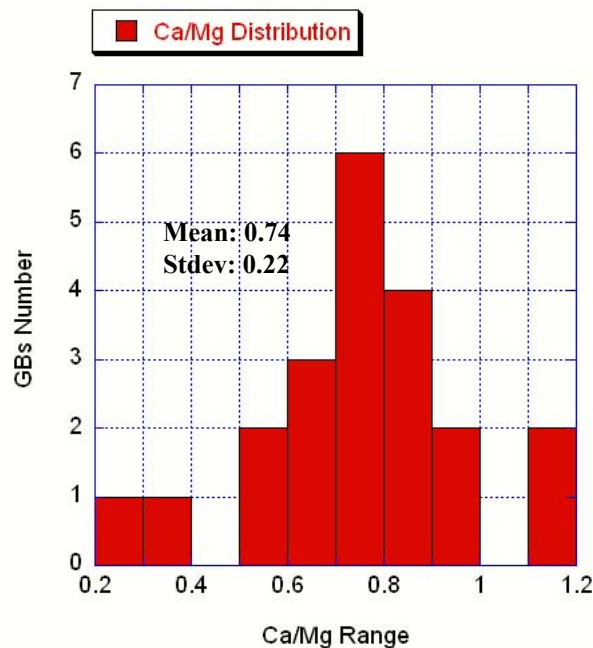
The image in Fig. 1(a) shows one of the boundaries that has been analyzed. The location of the position where the composition was repeatedly measured is denoted by an x. The histogram below (Fig. 1c) shows the distribution of these measurements. The image in Fig. 1b shows the ten different locations that were used to measure compositional uniformity and the histogram below (Fig. 1d) shows the distribution of composition. This measurement was carried out at five different boundaries and in each case, the data were used to determine a mean and standard deviation of the Ca/Mg ratio. These values are reported in Table 1. The results show that the uncertainty of the Ca/Mg ratio at a single point is between 5 and 10% of the mean value. When the measurements are made at multiple locations on the boundary, the scatter is somewhat larger. In the case of grain boundary 3, it is nearly 40%. We assume that this is because the grain surfaces are not strictly planar. On each boundary there is a slight curvature and near heterogeneities such as the pore shown in the boundary in Fig. 1, the change in the orientation of the surface normal can be larger.

**Table 1.** Comparison of the single point and multipoint scatter in measurements of the Ca/Mg ratio on different boundaries.

	GB1		GB2		GB3		GB4		GB5	
	SP	MP	SM	UC	SM	UC	SM	UC	SM	UC
<b>Mean Ca/Mg ratio</b>	0.59	0.58	1.11	1.13	0.25	0.24	0.33	0.34	0.53	0.60
<b>Standard Deviation</b>	0.05	0.08	0.06	0.16	0.06	0.09	0.04	0.05	0.07	0.13

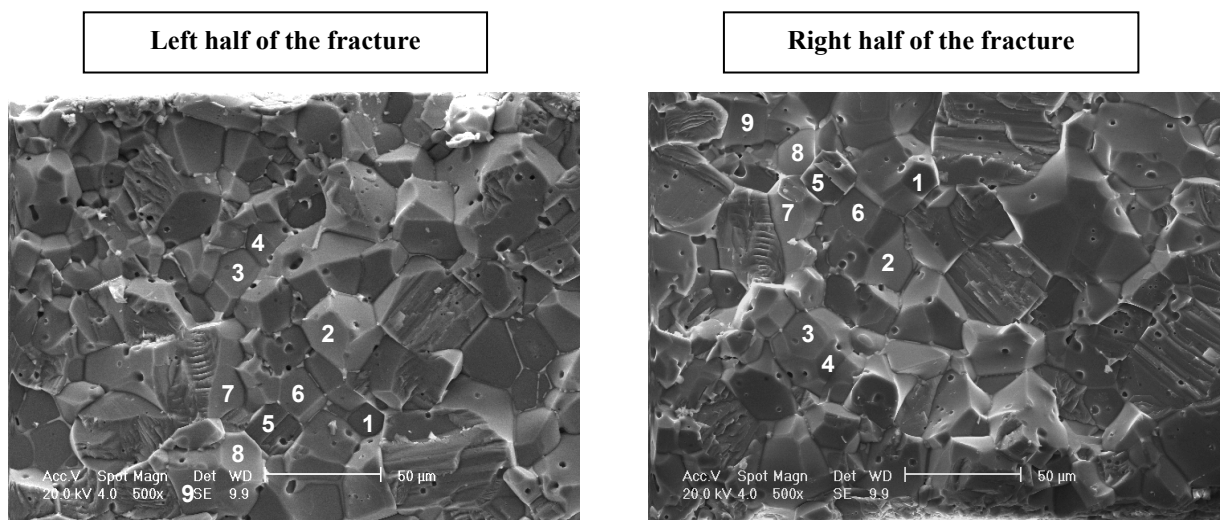
SP = single point scatter      MP = multipoint scatter

**Anisotropy of GB composition.** The Ca/Mg ratio on 21 different grain boundaries was measured by the multipoint sampling method described above. A histogram of these results is shown in Fig. 2. The figure shows the existence of significant anisotropy of GB composition; the Ca/Mg ratio varies by a factor of six. Thus, changes in the GB character can produce large GB composition differences.



**Fig. 2.** Distribution of the Ca/Mg ratio on 21 GBs in a Ca-doped MgO.

**Comparison of the compositions on both sides of a GB fracture.** Fig. 3 shows two sides of a fracture surface, with a certain number of GB facets identified on the "left" and "right" sides. The Ca/Mg ratios, as well as the standard deviations of both sides of each GB, are listed in Table 2. Although several GBs have compositions that are the same on both sides of the fracture, within one standard deviation, 2 of the 8 boundaries (GB3 and GB7) show significant composition differences between the two sides. The existence of such differences has been predicted by a recently developed model of GB composition which accounts for all five macroscopic parameters of GB character [11]. These differences also imply that intergranular fracture in MgO does not follow a zigzag path, but that GB's tend to fracture in a manner which preserves the identity of the surfaces which terminate the grains on either side of the GB.



**Fig. 3.** Reconstitution of the left and right halves of the fracture surface, showing the matching sides of set of GBS (from GB1 to GB9). This SEM picture has been taken after all Auger measurements were completed.

**Table 2.** Compositions of the left (L) and right (R) hand sides of eight different grain boundaries

LEFT	GB1L	GB2L	GB3L	GB4L	GB5L	GB6L	GB7L	GB8L
<b>Ca/Mg</b>	0.77	0.81	0.62	0.70	0.77	0.92	0.83	0.79
<b>STDEV</b>	0.14	0.08	0.06	0.12	0.12	0.30	0.08	0.06
RIGHT	GB1R	GB2R	GB3R	GB4R	GB5R	GB6R	GB7R	GB8R
<b>Ca/Mg</b>	0.70	0.66	1.19	0.83	0.71	0.93	0.57	0.86
<b>STDEV</b>	0.10	0.18	0.17	0.26	0.18	0.52	0.05	0.12

## Summary

There are measurable differences in the Ca/Mg ratio at different positions on grain surfaces. However, these differences are small in comparison to the variations from boundary to boundary. The Ca/Mg ratio varies by a factor of six on the different boundaries. Since the grain boundaries all show some curvature, the variations on a single boundary are probably due to variations in the orientation of the boundary. The more drastic boundary to boundary variations in the composition might also be caused by differences in the surface orientation, but it is also likely that the lattice misorientation plays a role. The influence of the boundary plane orientation on the composition is best illustrated by the fact that the two surfaces adjacent to the same boundary sometimes show different compositions, in agreement with a recently formulated model of GB composition as a function of GB character.

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