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TRANSMISSION ELECTRON MICROSCOPY STUDIES OF GRAIN BOUNDARIES IN CERAMICS

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Abstract. - TEM observations and diffraction studies obtained at grain boundaries (GB) in ceramic oxides are reviewed. For cubic oxides (e.g. MgO, NiO,...) some experimental observations reveal that the structure of their grain boundaries is similar or even equivalent to the structure of GB in cubic metals. The observable differences must be caused mainly by the ionic nature of these oxides.

A special imaging technique (defocusing imaging) was used to study the core region of GB dislocations. The observations suggest that at the GB dislocation there exist an electrostatic potential and an associated space charge. The influence of impurities on the electrostatic potential and the associated space charge is reported.

Only a few systematic observations on GB structure are available for oxides with a more complicated crystal structure, e.g. Al₂O₃. Only small angle GB were studied.

1. Introduction. - Similar as in metals, also in ceramic materials the grain boundaries and regions between grains and phases have an important, sometimes controlling, influence on many properties of the materials. Especially the mechanical properties (fracture strength, toughness, deformation, and high temperature creep) depend strongly on the structure of the grain boundaries, impurities at grain boundaries, and on the presence of intergranular phases.

Despite many experimental and theoretical efforts not too many results are known about the structure and properties of ceramic grain boundaries. Kingery (1) pointed out that from a purely phenomenological viewpoint, grain boundaries should have many similarities in metals and nonmetals. Grain boundaries in all classes of materials have an interfacial energy, they have a mobility which can be influenced by impurities, diffusion is usually more rapid along grain boundaries, deformation may occur by grain boundary sliding, segregation of solutes happens at grain boundaries, and grain boundaries act as sinks and sources for point defects.

But there exist important differences (Kingery (1)) between metals and ceramics which influence the structure and the properties of grain boundaries:
(i) The charges of the ions in ionic materials influence the stability of grain boundaries. (ii) The ionic bonding of ceramics (oxides, carbides, nitrides,...) leads to the formation of an electrostatic potential on grain boundaries which depends strongly on defect structures, impurities, and temperature; there is no analogy in metals. (iii) The impurity content in ceramics is usually much higher than in metals in which basic studies on structure and properties of grain boundaries are performed. (iv) In many ceramics, the energy of formation for point defects is extremely high (up to 7 eV). Therefore, the intrinsic defect concentration is just $10^{-9}$ at 1800°C, factors lower than the impurity level in the purest samples. In metals the reverse is usually reached. In addition, defects (vacancies and interstitials) may be charged which complicates the formation and stability of the defect. (v) In ceramic oxides (especially oxides of transition metals) deviation from stoichiometry occurs which leads to a temperature and oxygen pressure dependence of the composition, often oxides may have a large fraction of vacant lattice sites.

From those differences it must be concluded that, even since many similarities in the properties of grain boundaries in metals and ceramics exist, "arguments by analogy are often dangerous and unconvincing" (Kingery (1)).

For the investigations of grain boundaries in ceramics it is therefore essential that besides structural studies also the chemical composition at grain boundaries can be determined with high resolution; atomic resolution is desirable. The requested resolution is approached best by the different techniques of transmission electron microscopy (TEM), such as diffraction contrast techniques (2-5), high resolution TEM (6), diffraction studies (7), and analytical electron microscopy with high spatial resolution (8, 9).

In this paper a new technique will be presented which allows the detection of the change in mean inner potential at dislocations in grain boundaries. The effect is observed at grain boundary dislocations in nickel oxides. From the results of those studies conclusions can be drawn on the atomic structure of the region close to the dislocation or close to the grain boundary. In the following sections mainly TEM observations on grain boundaries in ceramic oxides will be described and compared with theoretical results. However, first of all, some comments recall the structure of ceramic oxides.

2. Structure of Ceramic Oxides. - Most of the simple metal oxide structures can be built up on the basis of nearly close-packed oxygen ions, with cations placed in available interstices; this is shown for a large number of structures in textbooks on ceramics (e.g. Kingery et al. (10)). Many oxides crystalline in the cubic rock salt structure, illustrated in Fig. 1a. In this structure the large oxygen anions are arranged in cubic close-packing and all the octahedral interstitial positions are filled with cations. Oxides having this structure are MgO, SrO, BaO, CaO, MnO, FeO, CoO, and NiO. Many studies on the structure of grain boundaries were performed in MgO, CoO, and NiO. There exist important differences between the latter three oxides. Magnesium oxide stays under all conditions (temperature, oxygen partial pressure) at stoichiometric composition. Most properties of MgO polycrystal-

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Fig. 1a: Cubic crystal structure of magnesium oxide (rocksalt structure) 
Fig. 1b: Cubic crystal structure of spinel (see text for explanation)
line specimens are controlled by impurities (11) since the energy of formation of
point defects as well as the ionization energies of the cations are very high. The
crystallography of NiO and CoO, as well as other oxides of transition metals,
depends as it is well known (11), on temperature and oxygen partial pressure. The
actual composition should therefore be written as e.g., Ni$_{1-y}$O. For NiO $y$ will be
$\sim 8 \cdot 10^{-5}$ at 1500°C and 1 atm. O$_2$. In CoO the concentration of the predominant
point defects is 10–100 times higher than in NiO. Therefore, it may be easier to
observe intrinsic properties in CoO than in NiO.
In MnO, FeO, CoO, and NiO an antiferromagnetic ordering of the magnetic moments of
the cations has been observed (12, 13) if the temperature lies below the Curie
temperature $T_c$. $T_c$ lies at 523 K for NiO. With this antiferromagnetic ordering a
change in structure is connected: those oxides change to the rhombohedral crystal
structure by a contraction perpendicular to a $<111>$ direction. The rhombohedral angle
deviates only by a few minutes from 90°. Boundaries between different magnetic do-
 mains can be observed either by TEM (14, 15) or by neutron diffraction studies (16).
ZnO crystallizes in the wurtzite structure which is a hexagonal close packed
structure where four oxygen ions are coordinated to each metal ion. The oxygen ions
are packed hexagonal with half the tetragonal interstices filled with the metal ions
so as to achieve maximum cation separation.
A number of oxides of the general formula AB$_2$O$_4$ have a cubic structure, shown
in Fig. 1b. The structure can be thought of as eight octants of alternating A$_8$
tetrahedra and B$_8$O$_4$ cubes as shown in the left part of Fig. 1b. The 4 oxygen ions
have the same orientation in all eight octants and so built up into a face centered
cubic lattice of 32 ions which coordinate A tetrahedrally and B octahedrally. As can
be seen from Fig. 1b, the complete unit cell possesses the composition A$_8$B$_4$O$_{12}$ (the
location of only 2 of B$_8$O$_4$ cubes is shown in the right part of Fig. 1b for orienta-
tion).

The more complex structure of Al$_2$O$_3$ is shown in Fig. 1c (17). In Al$_2$O$_3$ the pre-
ferred coordination number for aluminium is 6 so with a valence of 3 there is a bond
strength of one-half. This requires four Al$^{3+}$
ions adjacent to each oxygen ion which is a-
chieved by nearly hexagonal close-packing of the oxygen ions with aluminium ions filling two-
thirds of the octahedral sites. Subsequent simi-
lar layers are built up such that maximum spac-
ing of the Al$^{3+}$ ions is achieved.
Other important ceramics such as ZrO$_2$, HfO$_2$,
UO$_2$, as well as ThO$_2$ and TeO$_2$, have a fluorite structure due to the large size of cations. The
fluorite structure exists of a cubic packing of the oxygen ions with the cations in half of the
available sites with eightfold coordination.
There exist a large void in the center of the
unit cell.

More complex oxides such as olivines

\[ [(\text{MgO}, \text{FeO})_2 \cdot \text{SiO}_2], \text{forsterite} \]

\[ [(\text{MgO})_2 \cdot \text{SiO}_2] \text{ and enstatite } [(\text{Mgo} \cdot \text{SiO}_2] \]

possess even more complicated structures (c.f.
Wells (18)). In the case of one modification of
enstatite Si$_2$O$_3$ chains are formed.

The different structures were presented in some details to show that - compared to metals
which usually crystalline in very simple struc-
tures - additional structural difficulties may arise to form stable grain boundaries:
It must be assumed that additional problems due to charging, bonding, defect forma-
tion, etc. may occur, in those cases where a structural unit can not be completed
at the grain boundary.

3. The Detection of the Change in Mean Inner Potential at Dislocations and Grain
Boundaries. - When dislocations at grain boundaries are studied with transmission
electron microscopy, the techniques used such as strong beam (2, 3), weak beam, and
lattice imaging (2, 3), rarely provide information about the region in the vicinity

Fig. 1c: Structure of Al$_2$O$_3$
(c.f. Kronberg (17))
of the dislocation core. An experimental technique that is sensitive to the local environment at the dislocation core would be quite valuable, since, for example, it could be used to measure the change in density, to detect segregation and in the case of ionic solids, to detect the charge at the dislocation core.

In this section results are described of a study using such a technique (19). Experimental studies on edge dislocations oriented parallel to the electron beam in grain boundaries of NiO revealed that the sign of the contrast depends on the exact position of the image plane of the objective lens relative to the lower foil surface (defocusing imaging). The contrast behavior is similar to that observed from small cavities in a thin foil (Röhlle and Wilkens (20)). It can be assumed that the projected mean inner potential \( V_0 \) is changed close to the core of the dislocation. The change in \( V_0 \) causes a shift of the phases of the transmitted electron waves. The phase difference can be detected from the contrast behavior in different defocusing modes. Bursill et al. (21) have used this technique also to examine thin platelets in diamond.

3.1 Experimental Observations. - Thin foils (with small wedge angles) of NiO containing grain boundaries were prepared by an extremely careful polishing procedure and subsequent ion thinning. The TEM studies were performed in a Siemens Elmiskop 102 operated at 100 kV. The specimens were aligned in the microscope so that the dislocations associated with the grain boundary were exactly parallel to the incoming electron beam. The orientation relation between the normal on the lower foil surface and the incoming electron beam was also determined.

Fig. 2 is an image in a slightly overfocused condition which shows the full length of a 12° tilt boundary in NiO, when viewed along the tilt axis. The tilt axis is parallel to the \([104]\) direction. The boundary is clearly faceted along the \([100]\) direction and displays image contrast in the form of black spots of different intensities surrounded by faint white rings. The spot spacing can be measured, it is between 1.2 nm and 2 nm and the spot diameter is as small as 0.6 ... 0.7 nm.

S.L. Sass (unpublished research) demonstrated from tilting experiments that each of the spots corresponds to a dislocation which is being viewed end on Fig. 2. Fig. 2 also shows that the image contrast is low in the thin part of the foil and increases with increasing foil thickness. From the dependence of the contrast on the orientation as well as on the foil thickness (Fig. 2) it could be concluded that the observed contrast was not caused by artifacts, e.g. etch pits.

The Burgers vectors of the different dislocations were determined by utilizing Bollmann's theory (22). Results of the evaluations are summarized in Fig. 3. It was found that the plane of the grain boundary is a plane with a high density of coincidence lattice sites, the sites of the dislocations concur with the regions of worst matching. Bollmann's theory predict the sum of Burgers vectors in one facet. For the evaluation it was assumed that the dislocations in the small angle grain boundary possess a Burgers vector \( b \) (or multiple of \( b \)) of a lattice dislocation which is \( b = a/2 \{110\} \) (\( a \) = lattice parameter). It is found that the features possessing a strong contrast ("large dots") are dislocations with \( b = a \{100\} \), whereas the weak dots have Burgers vectors of the type \( a/2 \{110\} \) (Vaudin et al. (23)).

The dislocations were imaged under different focusing conditions, that means,
Fig. 3: Burgers vectors of the dislocations in a facet of the grain boundary of Fig. 2 \( (\gamma =+1, b) \cdot b_1 = a \ [100] \), \( \gamma_1 = 76^\circ \); \( \bullet b_2 = a/2 \ [101] \), \( \gamma_2 = 55^\circ \);
\( \odot b_3 = a/2 \ [110] \), \( \gamma_3 = 80^\circ \); \( a \) = lattice parameter, \( \perp \) = direction of dislocation line. Indices in the figures refer to the 2 grains adjacent to the boundary (23).

the imaging plane of the objective lens does not coincide with the lower surface of the foil, c.f. Fig. 4. The depth of field of the microscope has to be larger than the defocusing value \( \zeta \). For \( \zeta = 0 \) the lower foil surface is imaged with the objective lens. A plane which lies closer to the objective lens than the lower foil surface is imaged for \( \zeta > 0 \), the reverse is true for \( \zeta < 0 \). In a focusing series the change in focus was 22 nm/step. In order to illustrate the behavior of the image contrast with change in focus, images for 5 selected focus values are shown in Fig. 5a-e. The complete focus series exists of 60 similar micrographs. Fig. 5 demonstrates that on going from the overfocused to the underfocused condition the image appearance changes from black spots surrounded by white rings to white spots surrounded by black rings. For a certain defocusing distance the contrast of the dislocations disappears for a limited region of the grain boundary corresponding to a certain thickness of the foil. It would be very important for the evaluation of the micrographs if the intensity distribution could be determined experimentally. This was not possible on the micrographs taken until now since the sizes of the dots on the micrographs are too small. However, the widths of the dots could be measured. In Fig. 6 the widths of the contrast dots are plotted as function of the defocusing distance. The widths were measured from the micrographs for different foil thicknesses and for the different dislocations of a facet (with different Burgers vectors, see Fig. 3) perpendicular to the direction of a facet. It was observed that the sign of the contrast changes at slightly underfocused conditions \( (\zeta < 0) \), the widths depend on the exact defocusing value.

3.2 Contrast Calculations. - For the interpretation of the observations a model is assumed (Fig. 7) where the mean inner potential \( \bar{V} \) along a tube (radius \( r_0 \)) parallel to the dislocation line is changed compared to the mean inner potential \( V_0 \) of the foil boundary in NiO (see Fig. 3, 4).

![Fig. 5: grain boundary in NiO (see Fig. 3, 4). Dependence of contrast on defocusing distance \( \zeta \). a)\( \zeta=-198\)nm; b)\( \zeta=-110\)nm; c)\( \zeta=0\)nm; d)\( \zeta=+110\)nm; e)\( \zeta=+198\)nm.]
Fig. 6: Width $d$ of the contrast figures of Fig. 3. $d$ is measured for different defocusing steps $\Delta Z$, $\Delta Z = 1$ corresponds to a defocusing value of 22 nm. $d_1$ corresponds to the outer diameter of the white (dark) central spot for positive (negative) contrast; $d_2$, $d_3$: outer diameter of the surrounding rings.

Fig. 6a: foil thickness $t = 13$ nm, Burgers vector $b_1 = a \langle 100 \rangle$;
Fig. 6b: $t = 13$ nm, $b_2 = a/2 \langle 110 \rangle$;
Fig. 6c: $t = 46$ nm, $b_1 = a/2 \langle 100 \rangle$. The width was measured perpendicular to the direction of a facet.

Fig. 4: Sketch of the geometry for the defocusing imaging technique. The depth of field has to be larger than the defocusing value $\xi$.

Fig. 7: Model for the interpretation of the results. For infocus imaging ($\xi = 0$) a pure phase contrast exists which can be transformed to an amplitude contrast by defocusing imaging.

perfect crystal. The phase object reveals, of course, no contrast visible on an infocus image. The phase object can be transferred to an amplitude object if it is imaged under defocused conditions. It was pointed out by Rühle and Wilkens (20) that the influence of defocusing can be calculated in the following three steps.

(i) The Fourier transform $\tilde{\psi}$ of the amplitude $\psi$ at $z = t$ ($t =$ foil thickness) is calculated by:
\[ \Psi(t, \mathbf{p}) = \int \psi(t, \mathbf{r}) \exp \left[ -2\pi i \mathbf{p} \cdot \mathbf{r} \right] d\mathbf{r} \]  

(1)

where \( \mathbf{p} \) is a two-dimensional vector parallel to the image plane in the Fourier space, \( \mathbf{r} \) is a position vector in the image plane \((x, y)\) plane itself. (ii) The amplitude of the Fourier partial waves, \( \psi(t, \mathbf{p}) \) have to be multiplied with a phase factor \( T(p) \) ("amplitude transfer function") which accounts for the mutual phase shifts of the Fourier partial waves propagating from the plane \( z = t \) to the plane \( z = t + \zeta \):

\[ T(p) = \exp \left[ -2\pi i k_0 \cdot W(p) \right] \cdot B(p) \]  

with

\[ W(p) = \frac{1}{k_0} \frac{P_x^2}{k_0^2} + \frac{1}{2} \frac{P_y^2}{k_0^2} - \frac{C_A}{k_0^2} \]  

(3)

where \( k_0 \) = wave vector, \( C_s \) = constant of spherical aberration, \( C_A \) = constant of axial astigmatism, \( P_x \) and \( P_y \) are the components of \( \mathbf{p} \) parallel to the \( x \)-axis and \( y \)-axis, respectively. \( B(p) \) is the aperture function which depends only on the shape and position of the objective aperture, see (20). In the following we assume that \( C_A = 0 \). (iii) To calculate the amplitude field \( \psi(t + \zeta, \mathbf{p}) \) at the plane \( z = t + \zeta \) we finally have to perform a Fourier back transformation:

\[ \psi(t + \zeta, \mathbf{p}) = \int \psi(t, \mathbf{p}) \cdot T(p) \cdot \exp \left[ 2\pi i \mathbf{p} \cdot \mathbf{r} \right] d\mathbf{p} \]  

(4)

The integral of eq. (4) has to be evaluated for different amplitude distributions \( \psi(t, \mathbf{r}) \) at the lower foil surface and different defocusing values. For the calculations it is assumed that the contribution of the axial astigmatism to \( W(p) \) in eq.(3) can be neglected. The influence of the spherical aberration has to be considered.

For all calculations it is assumed that only the phase of the electron beam is shifted with respect to the wave field of the perfect crystal, i.e. we neglect the scattering of the crystal itself. This approximation was justified by results of many beam calculations which showed that the Bragg scattering contribution of the crystal can be neglected (M. Nühle, unpublished research) for the imaging conditions selected for the studies of the grain boundary dislocations (Fig. 5, 6).

The variation of the amplitude in the core region of the dislocation can then be written:

\[ \psi(t, \mathbf{r}) = \exp \left[ 2\pi i k_0 \cdot t \cdot \frac{\Delta V(r)}{E} \right] \]  

(5)

(E = energy of the incoming electrons)

In eq. (5) it is assumed that the change of the mean inner potential \( \Delta V(r) \) is only a function of the distance \( r \) (rotational symmetry); the origin \( (r = 0) \) is situated in the center of the dislocation core. Two models were assumed for \( \Delta V(r) \)

- **model I**: \( \Delta V = \Delta V_0 \) for \( r < \rho_0 \)
  \[ \Delta V = 0 \quad \text{for} \quad r > \rho_0 \]  

(6)

- **model II**: \( \Delta V(r) = \Delta V_0 \exp \left( - \frac{r_0}{r} \right) \)  

(7)

where \( \Delta V_0 \) is a negative number which corresponds to the smaller mean inner potential in the center of the disturbed region at the dislocation core. For the evaluation of eq. (4) a subroutine for fast Fourier transformations is used.

Fig. 8 shows a typical result of the calculations. For Fig. 8 model I was used, the diameter of the column is 0.8 nm. From Fig. 8 it can be concluded that under defocusing imaging conditions a contrast is visible. For underfocused (overfocused) conditions, corresponding to \( \zeta = -200 \text{ nm} \) \((\zeta = +200 \text{ nm})\) in Fig. 8, a contrast figure is observed which consists of a central white (dark) spot surrounded by a dark (white) ring. These results agree with the observations, c.f. Fig. 5. It should be noted that the size of the central spot extends over the actual width of the disturbed column. The results of the contrast calculations suggest that it should easily be possible to measure the sizes of the central spot as well as the subsidiary contrast rings. The dependence of the contrast was calculated as a function of defocusing (Fig. 9), width of the disturbed column for model I and model II (Fig. 10), and magnitude of the change in mean inner potential \( \Delta V/V_0 \) (Fig. 11). Finally, in Fig. 12 the calculated change of the diameters of the central spot, \( d_1 \), and of the...
Fig. 8: Results of contrast calculations. Model I, box potential eq. (6). For underfocused (overfocused) imaging conditions, $\zeta = -200$ nm ($\zeta = +200$ nm) the contrast figure is put together by a central white (dark) spot surrounded by a dark (white) ring. $I_B$ = background intensity.

Fig. 9: Defocusing contrast of the disturbed core region of a dislocation. Dependence on defocusing distance $\zeta$. Foil thickness 46 nm. $I_B$ = background intensity. surrounding ring, $d_2$, are represented as a function of the defocusing distance.

3.3 Comparison Between Experimental Observations and the Results of Calculations. - The results of the calculations have to be compared with the evaluations of the observations for the determination of the parameters of the variation in the potential $\Delta V_0$ and $r_0$ (eq. (6) and (7)). It would be extremely desirable if the maximum intensity (compared to the background intensity) in the central spot could be determined directly. This is, however, not possible until now. Therefore, the evaluation is done by comparing the observed width of the contrasts (Fig. 6) with the results of calculations (c.f. Fig. 12) where the experimental conditions are adapted as good as possible. The values for $\Delta V_0$ and $r_0$ can be limited to a certain range, since those values are available for different foil thicknesses, different defocusing values and different dislocation configurations. A qualitative comparison between the observed (absolute) intensities for different defocusing values (Fig. 9, 10, 11)
Fig. 10: Defocusing contrast of the disturbed core region of a dislocation. Dependence on column diameter $2r_o$, model II. Foil thickness 46 nm.

Fig. 11: Defocusing contrast of the disturbed core region of a dislocation. Dependence on the magnitude of the change in mean inner potential $\Delta V/V_0$, $V_0$ mean inner potential of the perfect crystal. Model II.

Fig. 12: Defocusing contrast of the disturbed core region of a dislocation. Dependence of the diameters of the central spot, $d_1$, and of the surrounding ring, $d_2$, as a function of defocusing $\Delta z$. $\Delta z = 1$ corresponds to a defocusing distance of $\zeta = 22$ nm. $2r = 0.8$ nm, contrast, $c = (I - I_B)/I_B$, $I_B$ = background intensity.

Fig. 13: Concentration profiles across grain boundaries in polycrystalline NiO specimens. Segregation of Cr at the grain boundary is observed for the specimen which shows nearly no defocus contrast.
and foil thickness narrows the allowable values for $\Delta V_0$ and $r_0$ further down. Unfortunately, it is not possible to distinguish between the two different shapes of $\Delta V(r)$ (eq. (6) and (7)). We assume that model II is more significant, since one can assume that there should be no abrupt change in the potential.

With this restriction the best fit is obtained for the following combinations of $\Delta V_0$ and $r_0$ (model II, $\Delta V(r) = \Delta V_0 \cdot \exp \left[- \left(\frac{r}{r_0}\right)^2\right]$)

(i) dislocation $b_3 = \frac{a}{2} [110], \gamma = 80^\circ$

$\Delta V_0 = -(0.09...0.15)V_0$ \hspace{1cm} (8.1)

$r_0 = (0.32...0.25)\text{nm}$

(ii) dislocation $b_1 = a[100], \gamma = 76^\circ$

$\Delta V_0 = -(0.13...0.18)V_0$ \hspace{1cm} (8.2)

$r_0 = (0.32...0.25)\text{nm}$

3.4 Analysis of Data. - The results described in eq. (8) have to be related to the atomic structure of the grain boundary dislocations in NiO. Puls and Norgett (24) calculated by computer modelling the atomic core structure of edge dislocations in MgO. The results suggest that a (nonlinear) dilatation exists which decreases the density of ions in the core region of the dislocation. Equivalent computations for NiO by Puls (unpublished research, 1982) reveal that the dilatation results in a change of the mean inner potential. The change can be approached by eq. (7) using the parameters

$$\Delta V_0 = -0.05V_0 \hspace{1cm} (9)$$

for an edge dislocation with Burgers vector $b = \frac{a}{2} [110]$. The comparison between eq. (8) and (9) shows that the nonlinear dilatation of the core of the dislocation is not sufficient to explain the evaluation of the observation.

The residual change of the mean inner potential can be explained either by the influence of a space charge (1), change in composition of NiO at the core of the dislocation, or by impurity segregations.

Preliminary experiments propose that impurity segregation at the grain boundary dislocations influence the intensity of the defocusing contrast. For other boundaries of a different NiO polycrystal no defocusing contrast was visible, even for large defocusing values. It was assumed that impurity atoms were segregated at those boundaries. Therefore, the chemical composition across several boundaries was determined by analytical TEM with high spatial resolution. Qualitative EDS analysis (Fig. 13) show that chromium is a major impurity which can segregate at the boundary. A comparison with the defocusing experiments reveal that a high concentration of Cr at the boundary results in a very low defocusing contrast ($\Delta V_0/V_0$ very small).

It is hoped that experiments which combine the defocusing contrast method with high resolution electron microscopy and analytical electron microscopy should provide a deeper insight in the atomic structure of grain boundaries in metal oxides.

4. TEM Observations of Grain Boundaries in Ceramics. - Recently, several conferences on grain boundary phenomena in ceramics (25-27) emphasized the importance of the experimental and the theoretical determination of the structure of grain boundaries in this group of materials. As mentioned before, only few systematic studies were performed concerning the structure of grain boundaries. The results of TEM observations are reviewed in this section. Emphasis is put on results obtained at grain boundaries in metal oxides, however, some observations on silicon nitride are reported first.

4.1 Silicon Nitride. - Silicon nitride ($Si_3N_4$) crystallizes in two different hexagonal modifications (29). The compact ceramic ($\beta-Si_3N_4$ structure) has to be fabricated by a liquid phase sintering process from $Si_3N_4$ powders ($\alpha-Si_3N_4$ structure). Additives of different ceramics (e.g. MgO) facilitate the sintering by lowering the reaction
temperature. It could be demonstrated by different TEM techniques (lattice fringe imaging (29-31), dark field imaging (29, 32)) that a vitreous phase is present on all large angle grain boundaries, see Fig. 14. Pockets of the vitreous phase are formed at grain boundary triple points. In Fig. 14 lattice fringes are visible in both grains adjacent to the grain boundary. It can be seen that a vitreous phase is present at the grain boundary. The thickness of the layer is < 1 nm. No vitreous phase is present on small angle grain boundaries if the misorientation between the grains is < 5°, see Fig. 15. Furthermore, (Schmid and Rühle (33, 34)) showed that no vitreous phase exists on special large angle twist boundaries in silicon nitride ceramics.

The chemical composition of the vitreous phase at the grain boundary as well as the chemical composition of the crystalline specimen could be determined with a high spatial resolution by electron energy loss spectroscopy - EELS - (Rühle and Petzow (35)). The diameter of the analysed area is > 5 nm. Fig. 16 represents the EEL spectra taken from both, the crystalline and vitreous area of the Si$_3$N$_4$ specimen.

![Fig. 14: Vitreous layer on a grain boundary in Si$_3$N$_4$.](image1)

The evaluation of the data revealed that the sintering aid (MgO) precipitates in the vitreous phase at the grain boundaries. Furthermore, it is observed at different Si$_3$N$_4$ specimens that impurities, such as Ca, also segregate in the grain boundary phase. No impurities could be analysed until now in small angle grain boundaries and in special twist boundaries by EELS.

The vitreous grain boundary phase influences strongly the mechanical properties of the material. It is well established (28) that the softening of the vitreous phase is responsible for the enhanced creep at high temperatures (T > 1000°C). At room temperature the strength and the toughness of silicon nitride are very high. The fracture occurs along the grain boundaries. Palm and Greskovich (36) found that the strength and the toughness of the material decreased when the thickness of the vitreous film on the large angle grain boundaries is reduced. The observation of Palm and Greskovich (36) indicates that the fracture along grain boundaries is facilitated if no vitreous phase is present. Therefore, it can be concluded that a "clean" grain boundary in Si$_3$N$_4$ possesses a higher energy than a grain boundary covered with a vitreous film.

The high grain boundary energy could be caused by the presence of uncomplete structural units of Si$_3$N$_4$ near the boundaries. The "free" covalent bonds of the uncomplete structural units may destabilize the "clean" grain boundary. The structural units (unit cell) can certainly always be completed at the boundary if the
Fig. 16: EEL spectra for the crystalline (---) and the amorphous (· · · ·) region of a Si$_3$N$_4$ specimen (Fig. 14). The intensities of the inelastically scattered electrons are plotted against the electron energy losses. The positions of the K-edges at the characteristic energy losses are marked for the different elements. Fig. 16a: energy range 300 eV < ΔE < 700 eV; Fig. 16b energy range 1000 eV < ΔE < 2000 eV.

highly defected vitreous film is present.

4.2 Alumina. - Coble (37) reported that small additions of MgO inhibit exaggerated grain growth in Al$_2$O$_3$ and allow near theoretical density to be achieved. Therefore, commercial Al$_2$O$_3$ usually contains small amounts of MgO. There remains substantial lack of agreement on the mechanisms which suppress the grain growth, despite extensive studies. It is, however, well established that commercial Al$_2$O$_3$ contains small amounts of MgO which can be concentrated at boundaries. In commercial Al$_2$O$_3$ Carter et al. (38) investigated the structure of small angle grain boundaries by electron diffraction and TEM studies. A periodic array of closely spaced lattice dislocations can be found. The periodic dislocation array causes extra streaks in the diffraction pattern. The length of the extra streaks is a measure of the grain boundary thickness. The distance between the dislocations equals to the observed grain boundary thickness, a result which is in agreement with theoretical predictions for metals (38) relating the thickness of a boundary to the spacing between dislocations in the boundary. Fig. 8 of (38) suggests that there exists an edge-on dislocation a defocusing contrast similar as described in section 3. No analytical TEM studies were performed at those small angle boundaries.

An enrichment of MgO can be analysed on large angle grain boundaries. Vitreous phases were observed (38, 38a). At higher dopant levels, spinel forms on the grain boundaries (40). Krivanek et al. (41) observed that other impurities (e.g. titanium) segregate at the grain boundary. Mechanical measurements imply that the presence of a grain boundary phase results in good mechanical properties.

4.3 Electronic Ceramics. - Many electronic properties of electronic ceramics (ZnO, BaTiO$_3$) are governed by the concentrations of impurities at the grain boundaries as well as on the presence and chemical compositions of interface interphases (25, 27). The results of analytical TEM provided an essential progress in the understanding of the electronic properties. In a first approach it seems to be more important to know the distribution of impurities at the grain boundaries than detailed structural investigations of a clean impurity free grain boundary.

4.4 Cubic Zirconia. - Zirconia stays at room temperature in the cubic fluorite structure if a stabilizer (such as MgO, Y$_2$O$_3$, CaO) is added, c.f. (42). It remains partially stabilized (PSZ), if the amount of stabilizer remains smaller than a critical value. The microstructure of commercial PSZ exists of grains with a mean grain size of ~50 μm. In the grains tetragonal or monoclinic ZrO$_2$ precipitates were formed (Heuer (43)).

It was observed that the toughness and the strength of the polycrystalline PSZ is improved if small amounts of SiO$_2$ are added. (Those additions are often not declared by the producers.) A detailed study of the microstructure of different Mg-PSZ revealed that a crystalline grain boundary phase is present (M. Rühle, unpublished research). EELS studies imply that the grain boundary phases exist of forsterite (MgO)$_2$ · SiO$_2$ or enstatite MgO · SiO$_2$. Preliminary results imply that a
high concentration of defects is present in those interface phases.

From an applied point of view it would, therefore, be more important to study the structure of the interface interphase than the structure of a clean boundary in ZrO₂.

4.5 Olivine. - Ricoult and Kohlstedt (44) investigated small angle grain boundaries in olivine, an orthorhombic mineral of composition (MgFe₀.₁)₂SiO₄. The authors found by TEM imaging and diffraction techniques that the structural width of the grain boundaries is smaller by a factor of 4 compared to the dislocation distance of the small angle grain boundaries. The authors assume that the structural width is changed by the segregation of impurities at the boundaries.

4.6 Magnesium Oxide. - Extensive experimental and theoretical studies on grain boundaries were performed for MgO. The results will be reported in the following subsections.

4.6.1 Experimental Studies. - Twist boundaries on [001] planes have been studied by using small cubic MgO crystals which were produced as smoke by burning magnesium in air. Chaudhari and Matthews (45) found that the small crystals in the smoke stuck together to form bicrystals containing [001] twist boundaries, while Mykura et al. (46) deposited the small single crystals on a MgO [001] single crystal to form also the [001] twist boundaries. A subsequent examination of the distribution of twist angles showed a marked preference for high density CSL orientations as seen in Fig. 17 (for the definition of a CSL lattice see e.g. (47)). This result provides first evidence that high density CSL orientations are of low energy.

Sun and Balluffi (48) prepared bicrystals by welding single crystals of MgO together under high pressure and high temperature. The twist misorientation of the boundaries was near to high-density CSL misorientations. Stable grain boundaries were obtained if the welding pressure and temperature was high enough (Sun (49)). The grain boundaries were examined by TEM. Square networks of screw grain boundary dislocations were analysed in all those boundaries (Fig. 18). The measured spacings of the grain boundary dislocations are plotted in Fig. 19 as a function of twist angle. The dislocations accommodate the misfit of the twist angle to high density CSL orientations (low Σ values, c.f. (47)). The observations of Sun and Balluffi suggest that the results on large angle grain boundary structure in MgO are very similar to those obtained in metals.

Moriyoshi et al. (51) produced "natural" small angle grain boundaries (SAGB) in MgO by deformation and subsequent annealing of single crystals of MgO. TEM studies demonstrated that the SAGBs exist of a network of lattice dislocations. Twist boundaries around [100] are found and show a square network of dislocations if the direction of the incoming electron beam is parallel to the [100] direction. The SAGB plane was not determined. It was assumed that it is perpendicular to the direction of the rotation axis by which the twist boundary was formed.

Kingery and coworkers (52, 53) determined with analytical electron microscopic studies that impurities segregate on all grain boundaries in MgO. Kingery et al. (52, 53) used well characterized MgO, the purity of this material was better than that of different authors (48, 49, 51). The results of Kingery imply that at all
Fig. 18: Networks of intrinsic screw grain boundary dislocations in [001] twist boundaries. The dislocations accommodate misorientations from exact CSL orientations. The lines with strong contrast are caused by dislocations accommodating a tilt component (from Sun and Balluffi (48)).

grain boundaries in MgO impurities are present. In summary, the observations in MgO suggest that the structure of small angle grain boundaries as well as of large angle grain boundaries are very similar to those observed in metals. However, all large angle grain boundaries seemed to be decorated with impurities.

4.6.2 Results of Calculations. - The structures and energies of boundaries in metal oxides were calculated by Wolf and Benedek (54) and Wolf (55) by molecular static methods. All calculated boundaries possess an energy which is barely smaller than the free energies of the two (001) free surfaces, see Fig. 20. The authors obtain their boundary structures by (i) placing the two twisted perfect half crystals together and then (ii) allowing the atoms in the interface region to relax. The rather high boundary energies (Fig. 20) are due to the fact that the Coulomb binding of the adjacent crystals is nearly zero since just about as many unlike ion pairs attract each other than like ion pairs oppose across the grain boundary ("anticoincidences"). The binding at the grain boundary is, therefore, due to the rather weak van der Waals forces (55). The energies of all boundaries are very closely independent of \( \theta \), there exists no evidence for cusps in the \( E(\theta) \) curve, c.f. (56).

4.6.3 Comparison between Experimental Observations and Structure Calculations. - There seems to be little or no agreement between the observations on grain boundary structures in MgO (48, 49) and the results of structure calculations (54, 55). The observations of Sun and Balluffi (48, 49) strongly support the presence of cusps in the \( E(\theta) \) curve near high density CSL orientations. Those cusps are not predictable by computer simulation experiments until now. The differences can be caused by impurities and/or point defects at the grain boundaries. Kingery (1) pointed out that charge effects should make grain boundaries in the oxides...
susceptible to important segregation effects. The interaction of impurity ions with the boundary must always be considered as a possible additional mode of relaxation and method of stabilizing the grain boundary. As an example, Cowley et al. (57) showed that twins formed in MgO smoke do not nucleate and grow in a dry atmosphere but they will nucleate and grow in the presence of water vapor. A conceivable structure of the twin can there be modelled as consisting of a layer of Mg(OH)$_2$ (brucite structure) with MgO growing on either side. It must be assumed that impurities and defects present at cleaved and polished surfaces (Sun and Balluffi (48)) influence the stability of the grain boundary strongly. Of course, those defects and impurities will also modify essentially computer simulation experiments: "anticoincidences" can easily be removed by vacancies and impurities simultaneously present near the boundary. TEM observations in NiO give a hint that nature tries to avoid the high energy "anticoincidences".

4.7 Nickel Oxide. - NiO possesses the rocksalt structure (Fig. 1a). The exact composition of NiO depends on the $O_2$ partial pressure $p_o$ and on temperature $T$. In many experimental studies measurements of the bulk diffusion (e.g., 58), grain boundary diffusion (59, 60), electrical conductivity (61), X-ray and neutron diffraction (62) and of mechanical properties (e.g., 63) were performed as a function of $p_o$, $T$, and other parameters. In addition, the structure of point defects and defect agglomerates was computer simulated (64). NiO is rather well characterized by all those studies.

Schmid et al. (65) studied by TEM small angle grain boundaries (SAGB) which were formed by plastic deformation and subsequent annealing of single crystals. Tilt boundaries (Fig. 21) as well as twist boundaries (Fig. 22) were found. The geometry of the twist boundaries with twist axis $\omega || [100]$ was analysed in details. Surprisingly, the normal $n$ on the SAGB plane in Fig. 22 does not coincide with $\omega$. The normal $n$ directed parallel to a $[111]$ direction. For other $[100]$ twist SAGB $n$ was parallel to a $[110]$ direction, $n$ lied never parallel to $[100]$. Similar observations were found by Lim and Peterson (68). The geometry of tilt SAGB was completely analog to those of metals, differences were only found for the $[100]$ twist boundaries.

The difference is caused by the charge of the ions. If a twist component would exist on a $(100)$ plane, than ions of like charges would lie in close proximity across the SAGB ("anticoincidences"). This configuration is extremely unstable, since the repelling Coulomb force increases the energy of the boundary drastically. To prevent the "anticoincidences" the $\omega || [100]$ twist SAGB change their plane preferentially on a $[111]$ plane since those planes exist of atoms of only one type of charges, "anticoincidences" are excluded. If the SAGB stays on a $(110)$ plane, the influence of "anticoincidences" is reduced by the introduction of extraneous dislocations into the network and also by relaxation processes.

Lim and Peterson (68) analysed by TEM also a large angle $[100]$ twist boundary close to a $\Sigma = 5$ orientation (Balluffi et al. (56)). The plane of the grain boundary
was dictated by the welding process: The bicrystal was fabricated by the usual Balluffi technique (50, 56) at 1500°C and by a 5% plastic deformation. Faint parallel lines could be observed on weak beam dark field images of the grain boundary. It was suggested (68) that those lines correspond to a grid of secondary GBD similar as in MgO, see Fig. 18 (48, 49). However, Sass (unpublished research) showed at the same boundary (68) that the lines were caused by dislocations which accommodated a small tilt component of the grain boundary.

Dhalenne et al. (66, 67) measured the relative free energy of [001] and [110] symmetrical tilt boundaries in NiO at elevated temperatures, Fig. 23, 24. The results for the [001] boundaries are definitely inconclusive concerning the question of the existence of cusps. The curve for the [110] boundary, Fig. 24, possesses cusps for Σ = 3, 9, and 11 misorientations. TEM micrographs of those boundaries contain faint lines (66) and it is not unambiguously certain that the observed contrasts are due to dislocations.

Duffy and Tasker (69) have recently carried out molecular statics calculations of the structures and energies of [001] symmetrical tilt boundaries. The boundaries are stable and possess, in contrast to the [100] twist boundaries, energies which are much lower than the energies of the two free surfaces. The configuration of the stable Σ = 5 (θ = 36.9°) boundary is shown in Fig. 25a. This configuration can be compared with this suggested by Kingery (1) on a qualitative basis, Fig. 25b.

The calculations (69) show that Kingery's configuration (Fig. 25b) is unstable. By an inspection of Fig. 25a it is obvious that the reduction in energy has clearly been achieved by reducing the number of atoms of like charges which lie in close proximity.

![Fig. 23: Measured ratio of grain boundary free energy, γ_b, to surface free energy, γ_s, for [001] symmetric tilt boundaries in NiO at 1520°C as a function of misorientation θ. Data from Dhalenne et al. (66).](image)

![Fig. 24: Measured ratio of grain boundary free energy, γ_b, to surface free energy, γ_s, for [110] symmetric tilt boundaries in NiO at 1520°C as a function of misorientation, θ. Data from Dhalenne et al. (67).](image)
across the boundary ("anticoincidences"). The reduction was caused by the increase of the volume of the bicrystal.

The results of the geometry of [100] twist SAGB and of the calculations (69) for large angle boundaries support strongly the assumption that a "clean" boundary (without defects and impurities) is only stable if no "anticoincidences" are present.

The defocusing contrast described in section 3 suggested that the density in the core region of the grain boundary dislocation is reduced stronger than expected from the atomic configuration of an isolated dislocation. This additional reduction at the core region can be caused by a volume increase in the central region of the grain boundary as shown in Fig. 25a.

It is expected that impurities influence the charge distribution at the grain boundary. Therefore, it would not be surprising if impurities and defects influence strongly the atomic positions and dilatations close to the central region of a boundary.

5. Conclusions.

(i) The different TEM techniques allow the structural and chemical characterization of grain boundaries down to the atomic level.

(ii) Information on the change in mean inner potential at grain boundaries can be obtained by special TEM imaging techniques.

(iii) Computer simulations of the structure of grain boundaries for NiO and MgO show that the grain boundaries possess a very high energy (which is close to the energy of the two free surfaces) if ions of like charges lie in close proximity across the boundary. The density of those "anticoincidences" is highest on (100) planes for a [100] twist boundary.

(iv) Few "clean" impurity free boundaries were studied in NiO. The TEM analysis shows that [100] twist boundaries on (100) planes are avoided. The density at grain boundaries is lowered to avoid the "anticoincidences".

(v) Most large angle grain boundaries in technical ceramics are covered by an interface interphase which seems to improve the mechanical properties of the materials.

(vi) It is essential to analyze not only the structure of grain boundaries but also the chemical composition with high spatial resolution.

6. References.


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DISCUSSION

L. HOBBS: Your boundary dislocations have a screw component. Have you considered the effect of the possible existence of jogs (and their charge) along the dislocation on the inner potential measurement?

M. RUHLE: I am aware of this problem, of course, the evaluation is made for pure edge dislocations. I believe that the influence of jogs and their charge on the contrast behaviour is rather weak.

A. REVCOLEVSCHI: I would like to thank you for quoting our results on grain boundary energy in (100) and (110) tilt NiO boundaries and make a comment on your restrictions concerning the "facetting" of our groove as seen on SEM pictures which might cast some doubts on the validity of our measurements. I want to say that such pictures have been taken on very heavily thermally grooved samples which obviously are impossible to study either by optical interferometry or by the Talystep technique. Our measurements are usually carried out on slightly etched samples. Now concerning your objection that in such grooves there might be a big variation of the surface energy with respect to the energy of the reference surface of the samples I want to restate that the angles at the bottom of the groove are very large (∼150° or more) and the plane orientation of both sides of the groove is not very far from that of the (100) or (110) reference surfaces.

M. RUHLE: I still believe that your results may be influenced strongly by an anisotropy of the surface energy. The evaluation is made under the assumption that the surface energy is isotropic, but this is not the case for NiO. Nevertheless, I believe your experiments are very helpful, especially since your specimens contain rather clean grain boundaries. It should be possible to get many information on the structure of a clean boundary. Of special interest would be to measure the charge in mean inner potential.