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Sessile dissociation in the stoichiometric spinel MgAl₂O₄ (*)

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Résumé. — Les dislocations dans le spinelle MgO.ₙAl₂O₃ sont dissociées hors de leurs plans de glissement. On a pu déterminer les plans de dissociation par une analyse stéréographique minutieuse. On montre que pour le spinelle stoichiométrique (ₙ=1), les nombreuses dislocations coin, longues et rectilignes, laissées par une déformation faible sur les plans de glissement {110} sont dissociées dans le plan {110} perpendiculaire au plan de glissement avec une largeur de dissociation de l'ordre de 10 nm. Dans le cas du glissement {111}, les orientations préférentielles sont coin, vis et 60°. Les dislocations coin sont aussi dissociées dans le plan {110} perpendiculaire au plan de glissement {111} avec la même largeur ≈ 10 nm, tandis que les dislocations de caractère 60° sont dissociées dans un plan {100} avec une largeur de 7 nm environ. Ces dissociations, observées de façon répétée, sont caractéristiques du début de la déformation en fluage du spinelle stoichiométrique et ils expliquent les orientations préférentielles observées. Après ce faible glissement initial, toutes les dislocations sont gelées dans ces orientations et la déformation doit se poursuivre par montée pure.

Abstract. — Dislocations in spinel, MgO.ₙAl₂O₃, are dissociated out of their glide planes and precise determinations of the dissociation planes by stereographic analysis are reported. It is shown that for stoichiometric spinel (ₙ=1), the numerous, long and straight, edge dislocations left by a small strain on {110} glide planes, are dissociated in the {110} plane normal to the slip plane with a dissociation width of the order of 10 nm. For {111} glide, preferred orientations are edge, screw and 60°. Edge dislocations are also dissociated in the {110} plane normal to the {111} glide plane with a dissociation width of 7 nm approximately. These features, which are repeatedly observed, are a general trend in early stage of creep tests (slip) of stoichiometric spinel and they account for the observed preferred orientations. When all the dislocations are frozen in these orientations, further deformation has to proceed by pure climb.

Fig. 1. — Possible dissociations in spinels.

1. Introduction. — Dissociation has been expected in MgAl₂O₄ spinel because of the large Burgers vector (b = ½ <110> = 0.58 nm) in this material and high shear modulus (µ = 1.18 × 10⁵ MPa) which would give rise to very large elastic energies for perfect dislocations. Possible dissociations have been studied from a theoretical (crystallographic) point of view by Hornstra [1], who only considered glissile dissociations. He proposed two possibilities (see Fig. 1):

\[ \frac{1}{2} <110> \rightarrow \frac{1}{4} <110> + \frac{1}{4} <110> \text{ or } AB \rightarrow A\gamma + \gamma B \]  

(1)

this dissociation could occur in any densely packed glide plane, and

\[ \frac{1}{2} <110> \rightarrow \frac{1}{2} <211> + \frac{1}{2} <12\bar{T}> + \frac{1}{2} <211> + \frac{1}{2} <12\bar{T}> \]  

(2)

or

\[ AB \rightarrow Aa + a\gamma + \gamma b + bB \]

which would occur only in {111} planes.

(*) This paper is a part of the work done by N. D. in fulfillment of a thèse d'état dissertation.
(**) Associated to the C.N.R.S.
Another possibility was suggested by Doukhan and Escaig [2], also in \{111\} planes.

\[
\frac{1}{2} \langle 110 \rangle \rightarrow \frac{1}{2} \langle 211 \rangle + \frac{1}{2} \langle 12\bar{1} \rangle \quad \text{or} \quad AB \rightarrow AO + OB
\]

(3)

Dissociated dislocations have been observed by several authors [2 to 4], in magnesium aluminate spinels \(\text{MgO}.n\text{Al}_2\text{O}_3\) with various stoichiometries i.e. with various \(n’\)s \(> 1\), as well as in other spinel crystals like nickel ferrites [5]. In fact, only the first dissociation reaction into two colinear partials has been clearly characterized. Moreover, it has been increasingly obvious that after high temperature deformation, dissociation occurs in planes different from the glide planes in non-stoichiometric [6] or stoichiometric [7] magnesium aluminate spinels, as well as in nickel ferrites [8].

In this paper we report on precise determinations of the dissociation planes in stoichiometric Mg-Al spinels slightly deformed in uniaxial compression. It is unambiguously shown that, depending on the sample orientation, either \(\langle 110 \rangle \langle 110 \rangle\) or \(\langle 110 \rangle \langle 111 \rangle\) glide can be activated. In both cases, the dislocation substructures in the early stage of high temperature deformation consist of long straight dislocations with marked preferential orientations; these dislocations are dissociated out of their glide plane:

i) for \(\langle 110 \rangle\) glide, they are edge dislocations dissociated in the \(\{110\}\) plane perpendicular to the glide plane;

ii) for \(\langle 111 \rangle\) glide they are either edge, screw or \(60^\circ\). The edge dislocations are also dissociated in the \(\{110\}\) plane perpendicular to their glide plane, while the \(60^\circ\) are dissociated in a \(\{100\}\) plane.

2. Sample deformation and dislocation substructures. — Samples with two different orientations have been subjected to creep under uniaxial compression.

i) the compression axis parallel to \([001]\). In this orientation, \(\{110\}\) glide is favoured. After 0.3\% strain at \(T = 1\ 853\ K\), Berg-Barrett topographs show traces of the \{110\} glide planes (Fig. 2a).

ii) the compression axis parallel to \([110]\), which favours \{111\} slip. The largest Schmid factor for \{110\} glide system is 0.25, while it is 0.41 for \{111\}. Berg-Barrett topographic evidence of (111) and (111) glide is seen in figure 2b, after a very small deformation with the same conditions as above.

Note that creep runs were stopped at the very beginning of the deformation because, for larger strains (i.e. for longer times at high temperature), the dislocation substructure mainly consists of junctions in equilibrium configuration with their arms forming \(120^\circ\) stars. This substructure is typical of climb, the proportion of which becomes more and more important as the deformation proceeds [7].

The dislocation substructure at the beginning of the deformation exhibits long straight dislocation segments which in general belong to one of the activated glide systems.

For \{110\} glide they are long edge dislocations (Fig. 3a).

For \{111\} glide, one finds edges, screws and dislocations with a \(60^\circ\) character; they often form octa-
Typical dislocation substructures observed in T.E.M.
a) \{110\} glide, long edge dislocations lying in their glide plane (101); plane of the foil (100); b) \{111\} glide, octagonal loop in the glide plane; the character of the straight segments are edge, screw or 60° or 120°; plane of the foil (111).

gonal loops like the one in figure 3b. Moreover, one also finds frequently long, straight edge dislocations parallel to [110], with a Burgers vector \(\frac{1}{2}\{110\}\) parallel to the compression axis. These dislocations, which are not activated by the stress, lie at the intersection of the two activated \{111\} glide planes; they are probably formed by the reaction of two glissile dislocations.

In both cases the dislocation density is of the order of \(10^{12} \text{ m}^{-2}\) as far as these densities can be correctly evaluated by conventional T.E.M. investigation at 100 kV. In both cases also, dissociation is clearly seen in weak-beam conditions and the dissociation width, as projected on the plane of the micrographs, never exceeds 10 nm.

3. Weak-beam determination of the dissociation plane. — 3.1 THE METHOD. — The orientation of the dislocation line \(\ell\) is determined by standard stereographic methods. The thin foil is then tilted around an axis, which has to be as near as possible to \(\ell\), and the apparent dissociation width of the fault ribbon \(\delta\) measured on the weak beam micrograph at high and well calibrated magnification (M position on a Philips microscope). This operation is repeated for various tilt angles \(\phi\) ranging between \(-45^\circ\) and \(+45^\circ\) keeping unaltered the diffraction conditions, the diffraction vector \(g\), and the deviation \(s\) from the exact Bragg conditions. Of course, this needs for each tilt, a slight rotation of the thin foil in its plane (1). The experimental curve \(\delta = \delta(\phi)\) is then compared with the theoretical predictions for several possible dissociation planes. Let \(d\) be the true dissociation width in the assumed dissociation plane \(P\), one easily finds by elementary geometrical considerations (see Fig. 4a)

\[
\delta/d = \sin(d_p, l_p) \cos(d, d_p)
\]

where \(d_p\) is the projection of \(d\) onto the micrograph plane \(\Pi\) and \(l_p\) is the projection of \(\ell\) onto the same \(\Pi\) plane. The two angles \((d_p, l_p)\) and \((d, d_p)\) are evaluated for each tilt angle on a stereographic projection (Fig. 4b).

On the other hand, it is well known that, even for good weak-beam conditions, the intensity peak corresponding to the dislocation image is slightly shifted [9]. Thus for a dislocation dissociated in the plane

Fig. 3. — Typical dislocation substructures observed in T.E.M. a) \{110\} glide, long edge dislocations lying in their glide plane (101); plane of the foil (100); b) \{111\} glide, octagonal loop in the glide plane; the character of the straight segments are edge, screw or 60° or 120°; plane of the foil (111).

Fig. 4. — Principle of the determination of the dissociation plane \(P\); \(\Pi\) is the plane of the micrograph: a) projection of the dissociated dislocation on \(\Pi\); b) determination on a stereographic projection of the two angles used in equation (4).

(1) For this kind of experiment, the most appropriate microscope holder is the tilt-rotation holder (side entry) which allows the dislocation line \(\ell\) to be aligned in the vicinity of the tilt axis.
of the thin foil, there is a difference between the true
dissociation width \( d \) and the distance between the
images of the two partials \( d' \). This difference is a
function of the \( g \cdot b \) products and of \( s \). In our case,
the Burgers vectors \( b_p \) of the two partials are identical
and one has [9]:

\[
d' = \sqrt{d^2 + \frac{2}{C^2}} \quad \text{with} \quad C = \frac{s}{2 \pi} \cdot \left( \frac{b_p + b_{pe}}{2(1 - \nu)} \right)
\]  

(5)

where \( b_{pe} \) is the edge component of \( b_p \) and \( \nu \) is the
Poisson coefficient. For dissociation widths of the
order of 10 nm, the relative difference \( (d' - d)/d \)
is smaller than 2\% for \( s \geq 0.2 \text{ nm}^{-1} \) and the correction
given by equation (5) can be neglected when
compared to the other errors; especially, measurements of \( \delta \) at various positions along the dissociated
dislocation image give rise to errors of the order of at
least 5\%. These measurements are performed by
microdensitometry of the negative and this scatter
is indicated by small rods on the \( \delta(\varphi) \) in figure 5a.

3.2 Edge dissociated dislocations in \{110\} glide. — Foils with various orientations clearly indicate
that most of the remaining dislocations are long edges. For the study of their dissociation plane, the
best orientation of the thin foil was found to be parallel
to (100). The edge dislocations lie in this plane, they
are parallel to [010] and their Burgers vectors are
\( b = \frac{1}{2}[101] \) (Fig. 3a).

The apparent dissociation widths \( \delta \) have been
carefully measured by microdensitometry for various
tilt angles between \(-41^\circ\) and \(+47^\circ\), the weak beam
diffraction conditions being kept unchanged. A typical
experimental curve \( \delta = \delta(\varphi) \) is shown on figure 5a,
while the theoretical curves deduced from eq. (4) are
shown on figure 5b for the four low index planes
containing the dislocation line i.e. (100), (001), (101)
and (101). It is clearly seen that only (101) fits the
experimental curve. A number of repeated examples

![Fig. 5. — a) Apparent dissociation width \( \delta \) versus the tilt angle \( \varphi \).
b) Calculated curves \( \delta/d = f(\varphi) \) for the various low index planes containing
the dislocation line.](image)

![Fig. 6. — Series of weak beam micrographs of the same dissociated
dislocation for various tilt angles. They correspond to the experimental
points of figure 5a, labelled a, b... g \( g = 044, |s_\varphi| \approx 0.2 \text{ nm}^{-1},
w = |s_\varphi| \approx 17\).](image)
shows that the observed edge dislocations are dissociated in the (101) plane normal to their glide plane (101). Figure 6 shows a series of weak beam micrographs of the various dislocation for various tilt angles (2). They correspond to the measurements labelled a, b, c... in figure 5a. The true width of the ribbon is found to be $d = 10 \pm 1$ nm, the uncertainty coming from the slight variation of this width from place to place along the dislocation line.

This sessile stacking fault has a very low energy [8, 10, 11] because it does not affect the anionic sublattice; moreover the two half crystals on both sides of the fault are in twin configuration. Calculations by Veyssière et al. [8] also indicate that this sessile dissociation is the most stable fault in disordered spinels, which is the case of our samples because they have been deformed at high temperature, well above the order-disorder temperature

$$T_{OD} \approx 800 \, ^\circ C [12].$$

3.3 THE CASE OF $\{111\}$ GLIDE. — The same method has been used to characterize the dissociation planes of the various straight dislocation segments, like those of the octagonal loop in figure 3b. Another example is seen in figure 7, in which the loop lies in the (111) plane, with a Burgers vector $\mathbf{b} = \frac{1}{2}[01\bar{1}]$. The results there are as follows:

— the edge segment is parallel to $[21\bar{1}]$; it is dissociated in (011), a plane normal to the (111) glide plane, in the same way as the edge dislocations in $\{110\}$ glide. The true dissociation width is again approximately 10 nm;

— the $60^\circ$ segment is parallel to [110]; it is dissociated in (001) and its width is about 7 nm. This dissociation is again a sessile one, the fault vector $\frac{1}{2}[01\bar{1}]$ being now at $\Pi/4$ to the fault plane. It is to be noted that Lewis also found faults in MgO..nAl$_2$O$_3$ $(^3)$ with $\frac{1}{2}[01\bar{1}]$ vectors as here [3];

— the screw part of the loop is again quite straight, a behaviour reminiscent of a sessile splitting mode.

However no definite dissociation plane can be ascertained, due presumably to too small a splitting. A fault ribbon $((100)$ $\frac{1}{2}[01\bar{1}])$ might be possible here, because among the possible simple index planes containing the screw dislocation, this fault would be the least energetic (it corresponds to a twin boundary) [8].

These differences in width found in the above three cases cannot be accounted for only by the change in dislocation character, which would give simply for colinear partial Burgers vectors:

$$d_0 = \frac{\mu b^2}{8 \Pi \gamma}, \quad d_{90} = \frac{d_0}{1 - \nu}, \quad d_{60} = \frac{4 d_0 (1 - \nu)}{4 - \nu}.$$  

(6)

Given some value of the fault energy $\gamma$, with $\nu \approx 0.25$, this would lead to typical figures of $d_0 = 7.5$ nm, $d_{90} = 10$ nm and $d_{60} = 9.4$ nm. Therefore the stacking fault energy has to be different in each case. Indeed, from the calculations by Veyssière et al. [8, 11], it is seen that the fault associated with $60^\circ$ dislocations does not correspond to a very low fault energy. It occurs here simply because, given the ribbon orientation as [110], it is (with the loop plane itself) the only low index dissociation plane which keeps the stoichiometry unchanged; the two other possible fault planes, (110) and (111) would lead with the fault vector $\frac{1}{2}[01\bar{1}]$ to a composition change, i.e. a high fault energy, since the layer removed would have respectively either the composition AlMgO$_2$ (or AlO$_2$) or AlMg$_2$O$_4$ (or Al$_3$O$_4$).

Moreover, a detailed crystallographic investigation shows that the three preferred orientations observed generally in (111) glide fit with those directions which allow a sessile dissociation to occur in a low index plane, without any change in stoichiometry as in the above two fully characterized cases of the edge and $60^\circ$ dislocations.

Another observation is that, rather surprisingly, no constriction appears needed when the faulted ribbon shifts from one straight direction to another: it progressively changes from one splitting plane to the other, as shown in figure 8. This might mean that, at least locally at the bend, the fault could be not so sharply confined in only one plane, as it is usually thought in metals, but be rather spread within a few nearly atomic planes, as has been observed for dissociated antiphase boundaries in some ordered alloys like Ni$_3$Mo [13], in order to avoid high energy ionic neighbours.

(3) In his paper [3] Lewis does not give the precise value of $n$.  

(4) Spinel samples are slightly sensitive to the electron beam irradiation as it can be seen by the small damage which appears after some observation time (see for example Fig. 6). We have ensured that this irradiation has no effect on the dissociation width by measuring $\delta$ for the same tilt conditions at the beginning and at the end of the work.
Finally, the fine structure of the long straight, edge dislocations described in § 2, parallel to [110] with a Burgers vector $\frac{1}{2}[110]$, and which are not activated by the applied stress (parallel to the compression axis), has been investigated. These are presumably produced by attractive junctions of dislocations glissile in the two stressed {111} planes. It has been possible to resolve the extended core structure in some cases, under weak-beam conditions, as shown in figure 9.

There, a dissociation of such junctions into three partials is observed. They are not coplanar, as seen from their emergence points and from the different micrographs taken for various tilt angles. However, at present we do not know what the planes of the two ribbons are. The same dissociation in three partials was also observed in non-stoichiometric spinel, $n = 1.8$ (see Fig. 10). The corresponding dislocation lines are near to the intersection of two {110} planes which are the glide planes for $n = 1.8$. In this case again, the stereographic analysis indicates that the three partials do not lie in the same plane and these dislocations have probably been formed by junctions. Such long barriers should behave as strong intracrystalline obstacles during strain.

4. Conclusion. — It has been suggested recently that the appreciable differences shown by Mg-Al spinels in their mechanical behaviour, depending on their stoichiometry, could stem from the differences in the splitting mode of the slip dislocations in this series of oxides [7, 8]. It is therefore most important to investigate and to know as completely as possible their extended core structure for the various stoichiometries tested mechanically. The above observations state some of these features for the stoichiometric spinel $\text{MgAl}_2\text{O}_4$.

In the early stages of deformation, dislocations can slip on {110} as well as on {111} planes, depending on the Schmid factor. The basic observation is the dissociation off the glide plane in both cases, most of the time only in one of the planes {110} or {100}, the faults most frequently observed being here of the types $(011) \frac{1}{2}[011]$, $(001) \frac{1}{2}[011]$, and possibly $(100) \frac{1}{2}[011]$ for screws. It is to be emphasized that such features are observed here in quite numerous examples over the thin foil, as a general trend in early slip. As opposed to some observations reported in the literature for non-stoichiometric spinels ($n = 3.5$) with a larger strain [6], the above sessile dissociations keep the stoichiometry unchanged and make the two partials quite stiff and correlated in straight or polygonal shapes. In the case of a $(101) \frac{1}{2}[101]$ slip, only the edge direction [010] is found as the intersection.
between the glide plane and one of the above fault planes, (100) (001) or (101), so that only the edges (among the non-screw dislocations) can be frozen straight along in the glide plane. For a (111) \( \frac{1}{2} [011] \) slip in the other hand, polygonal loops can be formed at the different intersections with the glide plane, as shown in figures 3b or 7, along [211], [110], [101] or even [011] for the screws.

It is clear that such configurations should inhibit further slip, inasmuch as any motion of the fault out of its plane is difficult. For the \{ 110 \} \( \{ 110 \} \) slip in stoichiometric spinel, it has been demonstrated consistently [7] that early slip is followed by pure climb as a deformation mechanism once straight edges are formed; the dislocation configurations observed at larger strain are then quite different, and lie generally in any plane (either non-crystallographic or with high indices). Mechanical characterization is in progress for \{ 111 \} \( \{ 111 \} \) slip.

Non-stoichiometric spinels behave quite differently. Although they also exhibit sessile dissociations, they seem nevertheless to deform still by plastic glide, at higher rates, the slip dislocations moving on roughly in their slip planes and their partials moving more or less independently [6]. Therefore some motion of the faulted ribbons out of the ribbon plane seems to occur there, while it could not so occur when \( n = 1 \). This basic difference, at the origin of a different mechanical strength, might be accounted for by some spreading of the fault on a few nearby atomic planes, and by the cation ability to rearrange by some short range diffusion motion onto the fault plane (somewhat similar to the synchro-shear motions of Hornstra [1]) when enough octahedral vacancies are available, i.e. when \( n > 1 \), and resulting in the forward shift of the fault plane [14].

References


