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GRAIN BOUNDARIES IN POLYCRYSTALLINE ALUMINA

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Résumé - Une détermination statistique des types de joints de grains (spéciaux et généraux) est effectuée dans deux aluminas de différente pureté. Les caractéristiques des joints de grains sont analysées : présence de dislocations intrinsèques et extrinsèques, configuration facetée, indices (densité) des plans de joints.

Abstract - The types of grain boundaries (special or not) have been determined from a statistical point of view in two aluminas of different purity. Grain boundary characteristics are analyzed: presence of intrinsic and extrinsic dislocations, faceted configurations and indices (density) of the boundary planes.

In ceramics as well as in metals, the grain boundaries have an important influence on many properties of these materials, particularly mechanical and electrical properties. The properties that control the manufacture of ceramics (sintering, grain growth) not only depend on crystallographic structure of interfaces, but also may be strongly modified by segregated impurities.

One purpose of our research is the determination, from a statistical view point, of the types of boundaries (special or not), found in sintered aluminas. As yet, most studies have been performed on ionic materials of cubic structure as MgO and NiO, so the analysis of the structure of grain boundaries of a hexagonal material (boundary plane - faceting, defects) is of basic interest: it is our second purpose.

This paper sets out the first results obtained about grain boundary structure in two types of alumina. The first one is obtained from a powder of current purity, the second one is prepared from a high purity slurry.

Our description is based on the geometrical model of grain boundaries developed by Bollmann [1]. On the basis of this model relatively few studies exist in ionic materials as structural models are more complex than in metals. Furthermore, the charge of the ions influences the stability of the boundaries, and the presence of segregated impurities may contribute to this stabilization, as shown in a theoretical study [2]. With the development of X-Ray spectroscopy in A.E.M., the chemical composition of an interface may be determined; that constitutes the third aim of our work to proceed to localized analytical electron microscopy on grain boundaries those crystallographic parameters are well established.

I- EXPERIMENTAL

First alumina* (ref. A) has been obtained from powders (99% purity). It has been hot pressed at 1720°C under a pressure of 20 MPa, then heated at 1420°C for one hour.

A purer alumina* (99,99% purity) has been prepared from aluminium isopropoxide

* Thanks to Mr. BIND (ONERA) who prepared materials.

$\text{Al}(\text{OC}_3\text{H}_7)_3$. A slurry is formed by mixing 3 moles of isopropoxide, 0,07 mole of HNO_3 and 100 moles of deionized water. The slurry is calcined in air at 800°C . Cylindrical samples are made by hot pressing at 1800°C in vacuum under a pressure of 25 MPa for one hour. The material is then annealed at 1500°C for 24 hours to eliminate Carbon.

Alumina samples were cut using a diamond saw and mechanically polished to a thickness of about $80\mu\text{m}$. Thin foils were obtained by ion milling with a 5 kV operating voltage. Finally, samples were coated with a thin layer of carbon to avoid charging in the microscope.

Our study is based on a geometrical approach of the coincidence. Delavignette has developed a method to establish tabulated coincidences for the hexagonal system /3/. For any axial ratio c/a , the procedure gives the C.S.L. tables up to a maximum Σ value of 35. Σ is function of two integer parameters μ and ν such as $\mu/\nu = (c/a)^2$. In the case of alumina where $c/a = 2,73$, the closest $(\mu/\nu)^{1/2}$ value is equal to 2,739. This is due to the non exactly close packing of oxygen atoms. We must distinguish between the exact C.S.L.'s, which are common to all hexagonal systems and correspond to rotations around $[001]$ (written ΣN_{ex}), and near C.S.L.'s (written ΣN). If different C.S.L.'s characterized by the same multiplicity exist, a distinction is made by addition of a small letter a, b, c..., in the increasing order with the value of the minimum rotation angle description. For all tabulated Σ , there is at least one description with a rotation angle of 180° . Practically, among all the descriptions, the largest rotation angle is detected; its deviation from 180° gives a first idea about the possibility of coincidence. Then the corresponding rotation axis is compared with tabulated rotation axis; grain boundary plane indices are also determined.

II - RESULTS AND DISCUSSION

The differences between the microstructures observed in both materials can be attributed not only to the difference of purity but also to the manufacture which is not strictly the same. Alumina A has a well equilibrated microstructure and a typical grain size of $\approx 10 - 20\mu\text{m}$. Porosity is observed at some triple points and sometimes at grain boundaries. No second phase particle has been detected. Alumina B has a strong heterogeneous microstructure; porosity occurs in the coarsest grains. The investigations of grain boundaries were made in the regions of small grains with similar size. Facets are more numerous than in Al_2O_3 A and there are a lot of boundaries making about 90° dihedral angles, this last observation has been reported elsewhere in the case of highly pure alumina /4/.

Three types of results have been obtained :

- the distribution of grain boundaries of each type " special " or " general " in the polycrystals,
- the observation of intrinsic and extrinsic dislocation networks in several boundaries
- the occurrence of facets in some boundaries .

i) concerning the distribution of grain boundaries, in alumina A, among the 65 boundaries studied, 25 are special, including 21 close to a coincidence orientation, 2 small angles boundaries and 2 boundaries close to a basal twin orientation (this twin is special as it does not modify the oxygen sub-lattice). In alumina B, among 37 boundaries studied, 14 are special, including 11 close to a coincidence orientation and 3 low angle. We also found 3 boundaries described by a 120° rotation around an axis 54° from $[001]$. This rotation is analogous to the three - fold symmetry around $[111]$ in cubic crystals. They have been called elsewhere " tri- perpendicular " (or " orthoaxial ") boundaries /5/.

Although the quantities of analyzed grain boundaries are different in the two mate-

rials, it seems that more special boundaries occur in alumina B. In both cases, the relative number of special boundaries is important compared to those obtained in iron alloys with B.C.C. structure /6,7/. This result agrees with a recent work where sintered materials present more special boundaries than materials produced either by cold working and annealing, or by orientated solidification /8/. It may be also correlated to the fact that alumina has a compact structure; a great number of special boundaries was recently detected in nickel /9/. From this point of view, it seems that F.C.C. and H.C. materials exhibit similar behaviour.

ii) A detailed observation of the microstructure of both materials reveals the occurrence of one or two dislocations arrays in 12 boundaries, those crystallographical description is given in Table 1.

n°	experimental misorientation θ [UVTW]	nearest Σ	tabulated misorientation [UTVW]	deviation from UTVW	boundary-plane indice
1	179°50 [5052]	Σ 7	180° [5052]	$\Delta R = 2^\circ$	
2	178°50 [2131]	Σ 19(a)	180° [3121]	$\Delta R = 0^\circ 5$	(5140)
3	178° [3471]	Σ 11(b)	180° [10556]	$\Delta R = 6^\circ$	(1010)
4	180 [2025]	Σ 11(a)	180° [1012]	$\Delta R = 5^\circ$	(1012)
5	178°50 [1010]	Σ basal twin	180° [1010]	$\Delta R = 5^\circ$	(1010)
6	Low angle grain-boundary				
7	178° [5051]	Σ 11(a)	180° [5051]	$\Delta R = 1^\circ$	(1012)
8	180° [2530]	Σ 19(a)	180° [5230]	$\Delta R = 4^\circ$	(1123)
9	180° [10111]				
10	176° [4261]				
11	179° [1011]	Σ 7	180° [1011]	$\Delta R = 0^\circ 5$	
12	Low angle grain boundary				

Table 1 : Crystallographic description of grain boundaries which contain one or more dislocation networks.

We must emphasize that most boundaries are special. Only boundaries 9 and 10 seem "general", but we may notice the possibility to describe these boundaries with a rotation axis normal to rhombohedral planes (1012); it may be equivalent to the C.A.D. model well established in the cubic system. This hypothesis is supported by the visualisation of a pseudo-periodic network of extrinsic dislocations, never observed in a "general boundary" (cf. Fig. 1) /7, 10/.

In the boundary no 2, two dislocations networks are observed: a coarse network of extrinsic dislocations and a fine strictly periodic one of intrinsic secondary dislocations, the spacing of which is consistent with the deviation $\Delta\theta = 0^\circ 5$ from the C.S.L ($\Sigma = 19$) experimentally obtained (fig. 2).

iii) A great number of faceted grain boundaries has been observed (fig.3). This phenomena is well known in alumina but only few structural studies at the present time exist /5-11/. A crystallographic analysis of faceted grain boundaries in alumina A and B is detailed respectively in Tables II and III.

Fig.1 : Extrinsic dislocations network observed in the n° 9 boundary (cf. Table I).

Fig.2 : Fine network of secondary intrinsic dislocations (A) and coarser network of extrinsic dislocations (B) in a special $\Sigma = 19(a)$ boundary (n° 2 in table I).

Fig.3 : Facets in the A boundary (Table II) large facets are parallel to basal plane (0001).

Fig.4 : a) schematic position of ions O^{2-} and Al^{3+} in a symmetric tilt boundary $\Sigma = 11(a)$, $\theta = 35^\circ 10'$ $[1\bar{2}10]$. Symmetry plane is $(10\bar{1}1)$.
b) position of ions O^{2-} and Al^{3+} in the same asymmetric boundary. Boundary plane is parallel to $(10\bar{1}0)$ in one grain and to $(10\bar{1}2)$ in the other grain.

n°	experimental misorientation θ [UTVW]	nearest Σ	tabulated misorientation [UTVW]	deviation from UTVW	boundary-plane indices
A	179° [3140]	$\Sigma 12$ ex.	180° [43 $\bar{1}$ 0]	$\Delta R = 5^\circ$	(0001) & (0001) (11 $\bar{2}$ 6) & (11 $\bar{2}$ 8)
B	177°50 [28 $\bar{6}$ 1]	$\Sigma 12$ ex.	//	$\Delta R = 5^\circ$	(0001) (11 $\bar{2}$ 8) & (10 $\bar{1}$ 2)
C	179° [32 $\bar{1}$ 0]	$\Sigma 7$ ex.	180° [32 $\bar{1}$ 0]	$\Delta R = 4^\circ$	
D	179°50 [3140]	$\Sigma 13$ ex.	180° [43 $\bar{1}$ 0]	$\Delta R = 1^\circ 5'$	(0001) & (0001) (11 $\bar{2}$ 9) & (10 $\bar{1}$ 5)
E	178° [43 $\bar{1}$ 0]	$\Sigma 13$ ex.	//	$\Delta R = 6^\circ$	
F	179°50 [10 $\bar{1}$ 2]	$\Sigma 11$ (a)	180° [10 $\bar{1}$ 2]	$\Delta R = 1^\circ 5'$	(10 $\bar{1}$ 0) & (10 $\bar{1}$ 2)

Table 2

Crystallographic description of grain boundaries in alumina A which exhibit facets. (In the last column, for each boundary, the first line gives the indices of the coarsest facet in one and in the other grain; the second line concerns the small facet).

n°	experimental misorientation θ [UTVW]	nearest Σ	tabulated misorientation [UTVW]	deviation from UTVW	boundary-plane indices
A'	172° [25 $\bar{3}$ 1]	-	-	-	(0001) in one grain (0001) in the other grain
B'	176° [15 $\bar{6}$ 3]				(11 $\bar{2}$ 6) in one grain (0001) in the other grain
C'	178° [81 $\bar{7}$ 0]	$\Sigma 19$ ex.	180° [81 $\bar{7}$ 0]	$\Delta R = 5^\circ$	(0001) in one grain (10 $\bar{1}$ 3) in same grain
D'	171° [23 $\bar{1}$ 1]				(0001) & (11 $\bar{2}$ 3)
E'	176° [24 $\bar{2}$ 1]	$\Sigma 29$ (a)	180° [24 $\bar{2}$ 1]	$\Delta R = 3^\circ$	
F'	175° [1543]				(0001) in one grain
G'	Low angle				(0001) & (0001)

Table 3

Crystallographic description of grain boundaries
in alumina B which exhibit facets

In Alumina A, it is worth noting that among the 65 boundaries studied, only 7 boundaries are close to an exact C.S.L. orientation and 5 of them are faceted. In alumina B, only the boundary C' has a description near Σ Nex. For both samples, the coarsest facets are most often parallel to basal plane, which is the densest plane, and, in the case of Σ Nex., the plane of highest density of coincident sites. The case of F boundary is especially interesting. This special boundary $\Sigma = 11(a)$ can be described by a 35° , 10 rotation angle around $[11\bar{2}0]$. An attempt is made to get a detailed analysis of the crystallography of the largest facets, the figure 4(a) is a schematic description of a 35° $[11\bar{2}0]$ tilt boundary with a symmetric highly coincident plane. By moving some ions from one grain to the other, a facet (10 $\bar{1}$ 2) in one grain will lie parallel to a facet (10 $\bar{1}$ 0) in the other grain (fig. 4b), this is the experimental configuration observed for the largest facets.

In Alumina B, a high proportion of boundaries making a 90° dihedral angle exists. Of these, several are general but we must point out that in one grain, at least, their plane is a basal one.

III.- CONCLUSIONS

The first results in this study emphasize the occurrence of numerous special boundaries in two sintered aluminas (99 and 99.9% purity). Some boundaries contain networks of intrinsic and extrinsic dislocations that may be explained on the basis of the near coincidence. Facets observed in some boundaries lie parallel to densely packed planes in one grain at least. Work is now carried on with alumina, doped with various solutes to analyze the influence of the valency and the size misfit. STEM microanalysis will be performed parallel to structural studies.

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