Stoichiometry defect at grain boundary observed by nano-scale TEM microanalysis in spinel MgAl2O4

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Abstract.

It was already showed that spinel present a grain boundary sliding deformation accommodated by diffusion during creep at high temperature [1,2]. A space charge layer at grain boundary in ionic ceramics can explain the observed interface reaction controlling diffusion at low stress (less than 60 MPa). The nonstoichiometric area due to ionic defect should create an electrostatic potential between the grain surface and inside grain. This surface dipole region suppose an excess free energy necessary to form cation and anion vacancies [3, 4]. The purpose of this work is to study the grain boundary region stoichiometry to confirm this theory. Fine-grained spinel (average grain size under micron), which presents an interface reaction at low stresses, is studied by TEM nano-scale microanalysis. The cation ratio Al/Mg variation is well described. It varies from 2.5 at grain boundary to 2.15 at 100nm inside the grain. The ratio Al/O shows no variation across the grain boundary and suggests that the stoichiometry defect observed is due to an excess of magnesium vacancies located at the grain boundary.

Key words: Grain boundaries (B), Spinels (D), Electron microscopy (B), Defects (B), Space charge

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Introduction

The plastic deformation of near stoichiometric fine grain spinel is due by the grain boundary sliding accommodated by diffusion [1,2]. At low stresses, the stress exponent increases to 2. The Raj and Ashby [5] model is based on the diffusion flux of vacancies from the tensile boundaries which is the sink of mater to the compressive boundaries which is the source of matter. At low stresses, the interface reaction process, by which the vacancies are formed, limits the creep flow rate and causes an increase of the stress exponent.

In ionic compounds, the lattice defects are positively or negatively charged. The different free energies of formation of the anion and cation defects create a local electrical potential. Assuming that the major defects present in ceramics are vacancies, in equilibrium the grain boundary presents an electrical charge compensated by an opposite electrical charge cloud near the boundary called space charge. The space-charge region creates an electrical potential and so modified the conditions of the charged defects formation and diffusion that can explain the comportment of the spinel at low stresses.

Chiang and Kingery [6] have found an increase the cation ratio Al/Mg at the grain boundary and assume the existence of a charge cloud near the grain boundary. The aim of this work is to realize the quantitative microanalysis at the grain boundary to obtain the chemical concentration variation of each element and so to conclude or not the existence of such space charge cloud.

Experimental

A Hot Isostatic Press (HIP) of a commercial stoichiometric powder allowed obtaining a near dense spinel with an average grain size value of 0.61µm.

For the determination of the chemical composition, we used a STEM equipped with a windowless energy dispersive X-ray detector. Each analysis was performed using an electron beam spot accelerated at 300 kV. The microanalysis was performed at the sample area which the thickness never exceeds 175 nm.

Samples observed by TEM had been prepared using the South Bay Technology Tripod polisher. They are thinned mechanically to transparency by the polishing of both side. X rays analysis was performed by focusing the electron beam on the sample. The electron spot size was 5.61 nm and the widening in the thin region is negligible. To determine the chemical variation, the electron beam is translated along a line from one grain to its neighbor. The grain boundary crossed by this line is well parallel with the electron beam. The distance between two analyses is 20 nm. In figure 1, black points on the sample are due to the carbon contamination of the sample induced by the electron beam. We can note that each points are clearly separated with its neighbors, and so each analysis was not perturbed by the others analyses. Figure 2 shows an HRTEM micrograph. It reveals that the interface is free from vitreous phase.

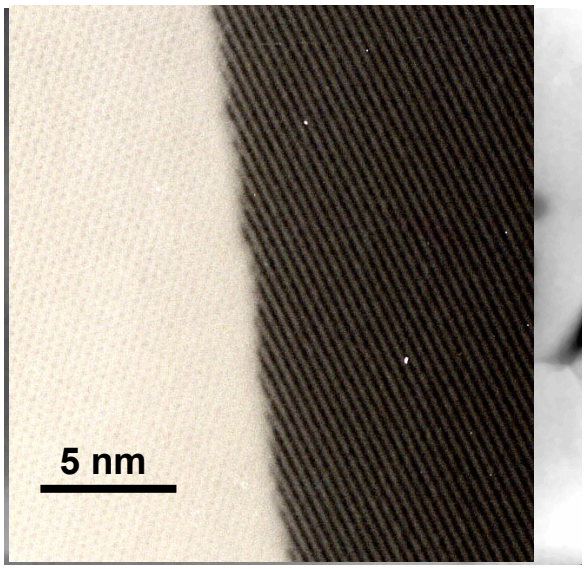

Figure 1. TEM picture of a HIPed spinel just after X-ray analysis.

Figure 2. HRTEM micrograph of a boundary

Results and discussion

The composition inside the grain has been easily determined to be $MgO\text{-}1.07Al_2O_3$. No impurity could be detected into grains and at the grain boundaries. As observed by Chiang and Kingery [6], at all grain boundaries examined, the Al/Mg cation ratio increased relative that of the bulk, as is shown in figure 3.

This figure shows that the O/2Mg ratio follows the variation of the Al/Mg ratio and no significant evolution can be noted for the O/Al. Therefore we can affirm that the observed change of the stoichiometry at the boundary is real and not due to an experimental error.

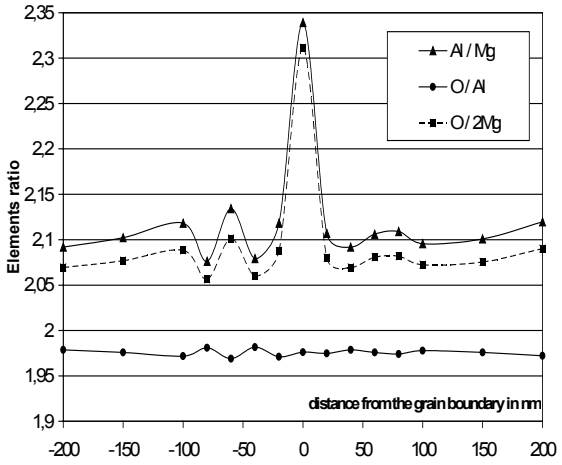

Figure 3. STEM segregation profile at grain boundary in spinel

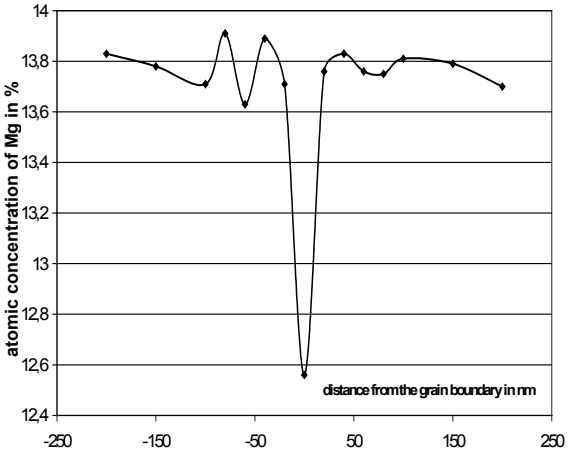

Figure 4. Evolution of absolute concentration of Mg across a grain boundary of a HIPed spinel

Sample prepared by the South Bay Technology Tripod polisher, present no variation of thickness at the grain boundaries. By the Doukhan and Van Capellen [7] method to determine the thickness, we achieved the absolute concentration of all elements present in the spinel. The figure 4 shows the evolution of Mg concentration across the grain boundary. It shows clearly that the stoichiometric defect at the grain boundary is due to a decrease of the magnesium concentration.

The profile of magnesium concentration and the variation of the differents ratio suggest an excess of Mg vacancies at the grain boundary. The consequence is an excess of negative

charge at the grain boundary compensate by a positive space-charge cloud near the boundary. Regarding the no-variation of the O/Al ratio, the excess of Mg near the grain boundary, and assuming that the energy to create oxygen vacancies must be important, the cloud space charge should be due to an excess of Mg interstitial defects.

Conclusion

The South Bay Technology Tripod polisher technique to prepare thin sample for TEM observation and the nano scale microanalysis avoids us to clearly characterize the stoichiometric defect present at the grain boundary in spinel. The X-ray analysis operated across the grain boundary has shown an increase of the Al/Mg and O/Mg ratio at the grain coupled with an unchanged O/Al ratio. This stoichiometric change suggests the existence of a positive space-charge cloud near the boundary. This space charge can explain why the interface reaction controlled the superplasticity flow at low stress by the change of the energy need to form charged defect in spinel

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