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LA-UR--89-2929

DE89 016969

TITLE INTERGRANULAR AND INTERPHASE BOUNDARIES IN CERAMICS

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SUBMITTED TO International Conference on Intergranular and Interphase
Boundaries in Materials, Paris, France, September 4-8, 1989

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INTERGRANULAR AND INTERPHASE BOUNDARIES IN CERAMICS.

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Resumé - L'effect des interfaces sur les propriétés des céramiques électroniques et structurales est majeur. La microstructure et la microchimie des interfaces peuvent être déterminées par microscopie électronique à transmission, à transmission, à haute résolution et analytique. Les exemples étudiés proviennent de céramiques contenant des joints de grains entre phases et intergranulaires. Les sertiens contiennent des joints de grains à bas angle, twin et à 90° dans des céramiques superconductrices $\text{YBa}_2\text{Cu}_3\text{O}_7$. Les joints de grains entre phases contiennent des couches épitaxiales de $\text{YBa}_2\text{Cu}_3\text{O}_7$ sur des substrats de SrTiO_3 et de LaGaO_3 ainsi que des interfaces non orientées communément décrites dans les coatings et les composites.

Abstract - Interfaces are of great importance in both electronic and structural ceramics. The microstructure and microchemistry of interfaces can be studied by transmission electron microscopy, both high resolution and analytical. Examples are taken from both intergranular and interphase boundaries in ceramics. The former include low angle, twin and 90° boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductors. Interphase boundaries include epitaxial layers of $\text{YBa}_2\text{Cu}_3\text{O}_7$ on SrTiO_3 and LaGaO_3 , and non-oriented interfaces such as occur in coatings and composites.

1 - INTRODUCTION

Internal interfaces play a critical role in the physical and mechanical properties of ceramics. Such interfaces include both intergranular and interphase boundaries, which can also be termed homophase and heterophase boundaries. The first case encompasses grain and twin boundaries where there is only an orientation change. In the second case both the structure and orientation can change across the interface. There may be a special orientation relationship, as in epitaxially grown structures, or no orientation relationship at all, as in ceramic-ceramic composites. In both types of boundaries, segregation of impurities and boundary phases are common. Transmission electron microscopy, both high resolution and analytical, is one of the most powerful techniques for characterizing interfaces. Examples of such studies will be presented.

2 - EXPERIMENTAL METHODS

Interfaces in a variety of ceramic materials have been studied by transmission electron microscopy (TEM), as described below. For layered and coated materials both plan sections and cross-sections have been employed. Techniques for the preparations of cross-sectional TEM specimens are tricky and have to be tailored to the particular system. For example, epitaxially-grown layered systems tend to have good adhesion and can be prepared by standard sandwich methods /1/. On the other hand, coated systems such as zirconia thermal barrier coatings often have poor adhesion at the interface and need special handling for mechanical thinning and ion milling /2/. Ion milling was performed on a Gatan ion mill equipped with a liquid nitrogen specimen cooler which is important for minimizing the damaged region in specimens for high resolution electron microscopy (HREM). HREM was performed on a Philips CM30ST with a point-to-point resolution of 1.9Å while analytical microscopy (AEM) was done on a separate CM30 equipped with a Kevex x-ray system.

3 - OBSERVATIONS AND DISCUSSION

(a) Grain and Twin Boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_7$
Twins are the most characteristic feature of the microstructure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ high

Fig.1:Twins in $\text{YBa}_2\text{Cu}_3\text{O}_7$ viewed along $[001]$.

Fig.2:Low angle tilt boundary in $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Fig.3:90° grain boundary in $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Fig.4:Cross-section through $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin film grown epitaxially on $(001) \text{SrTiO}_3$. Inset is a HREM picture of the interface.

temperature superconductors (Fig. 1). The twins help accommodate the shape change during the tetragonal-to-orthorhombic transformation /3/. In the early days of discovery the twins were thought to play an important role in superconductivity but now they are considered to provide only weak pinning for fluxons. HREM shows that the twin boundaries are atomically sharp /4/.

Grain boundaries are now recognized as being critical to the performance of the ceramic superconductors, acting as weak links and Josephson junctions in the superconducting behavior. The critical current decreases with increasing angle of misorientation /5/. A small angle boundary in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is shown in Fig. 2, where the individual dislocations making up the boundary are evident. The large c-axis Burgers vectors are dissociated by climb /6/. With increasing misorientation, the dislocations cores overlap and the boundary acts as a Josephson junction /6/. 90° boundaries are common in $\text{YBa}_2\text{Cu}_3\text{O}_7$, especially in thin films where grains with the c-axis perpendicular to the substrate habitually switch to a- or b-axis grains. An example is shown in Fig. 3; the 2% difference between a and c/3 is taken up with misfit dislocations. Presumably such boundaries present a severe obstacle for the supercurrent. The key to the commercialization of high T_c superconducting is texturing and the control of grain boundaries. In sintered ceramic superconductors, carbon from the BaCO_3 used in preparation has difficulty in escaping and is thought to lodge at the grain boundaries, deteriorating the critical current even further /7/.

(b) Epitaxial Growth of $\text{YBa}_2\text{Cu}_3\text{O}_7$ on SrTiO_3 and LaGaO_3

Thin films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ can be grown epitaxially on single crystal substrates by a variety of techniques, either in situ or post situ. In the present case films were deposited by electron beam heating of Y, Cu and BaF_2 targets followed by post situ annealing in wet O_2 (850°C for 1 hr) and dry O_2 (850°C for 2hr). A typical cross-section for a film grown on (001) SrTiO_3 is shown in Fig. 4. The misfit is quite small (2 % for the a-axis and 0.3% for the b-axis of $\text{YBa}_2\text{Cu}_3\text{O}_7$) and so the layer next to the substrate has its c-axis up. However, the thickness of this layer seldom exceeds $0.5 \mu\text{m}$ before the a and b orientations nucleate. The problem seems to be that the growth rate in the ab plane is much greater than along the c-axis. This is good for providing rapid coverage of the substrate with the first layer. However, if the 90° orientations subsequently nucleate epitaxially on the slow growing first layer, then the new grains can grow rapidly giving a blocky structure. Effectively the critical current carrying capacity is determined by the inner layer.

LaGaO_3 is orthorhombic (pseudo cubic) but has on the average a lower misfit with $\text{YBa}_2\text{Cu}_3\text{O}_7$ (0 to 1.9%). The inner layer is somewhat more perfect and tends to grow thicker (Fig. 5), but inevitably the orientation tends to flip, for the reasons given above. 90° grain boundaries are common in thin films, as shown in Fig. 3.

(c) Epitaxial growth of $\beta\text{-SiC}$ on Si

$\beta\text{-SiC}$ is the metastable cubic sphalerite form of SiC and can be grown epitaxially on Si by chemical vapor deposition (CVD) /8/. This occurs in spite of the fact that the lattice parameter of $\beta\text{-SiC}$ (0.436 nm) is 20% smaller than that of Si (0.543 nm). Most of the difference is taken up with misfit dislocations at the interface, as shown in the HREM image of a cross-section in Fig. 6. Stacking faults, twins and threading dislocations are also nucleated at the interface and grow with the $\beta\text{-SiC}$ layer. Inversion domain boundaries (IDB's), also called anti-phase domain boundaries (APB's), are a common feature (Fig. 6). These are thought to nucleate at atomic steps on the surface of the Si such that the regions on either side of the step grow out of phase with the Si and C sites switched. All these types of defects are found in heteroepitaxial films grown on Si, regardless of the size of the misfit. It has been suggested that this is due to three-dimensional nucleation and faceting during the early stages of growth /9/. Control of this process is important for reducing the defect density in such thin films so that they can be made into useful wide band-gap devices.

(d) $\text{GaAs}/\text{Ga}_{1-x}\text{In}_x\text{As}$ Strained-layer Superlattices

The use of strained-layer superlattice as devices depends on their crystalline perfection after growth. In the present case superlattices were grown on (001), (111) and (111) GaAs substrates by molecular beam epitaxy (MBE). Each superlattice consisted of 20 periods of $70\text{\AA}$ of the $\text{Ga}_{1-x}\text{In}_x\text{As}$ well ($x = 0.10$) and $140\text{\AA}$ of the GaAs barrier, grown over a 300 nm graded buffer of $\text{Ga}_{1-x}\text{In}_x\text{As}$ /10/. The misfit between the lattices was less than 1%. A plan section shows a heavy dislocation density in the form of a triangular network for the (111) substrate (Fig. 7). Stereo microscopy

Fig.5: Cross-section through $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin film grown epitaxially on LaGaO_3 . A structure image of the interface is shown on the right.

Fig.6: Cross-section through $\beta\text{-SiC}$ grown epitaxially on (001) Si viewed along $[110]$ showing interface dislocations (D), stacking faults (F) and anti-phase boundary (APB).

Fig.7: Plan view of (111) $\text{Ga}_{1-x}\text{In}_x\text{As}/\text{GaAs}$ strained layer superlattice (SLS).

Fig.8 Cross-section through SLS of Fig. 7 showing (a) dislocation network at the substrate (S) buffer (B) interface and (b) threading dislocations in the SLS.

shows that the network is mostly planar with some dislocations moving into and away from the substrate. Cross-sectional specimens are more revealing (Fig. 8). The network dislocations lie almost entirely at the buffer substrate interface with some movement of dislocations into the substrate and occasional threading dislocations penetrating into the superlattice. Diffraction contrast analysis shows that most of the dislocations have $\frac{1}{2}\langle 110 \rangle$ Burgers vectors out of the plane of the substrate and thus nucleate and move in response to the plane stress due to the misfit /11/.

(e) $\text{Si}_3\text{N}_4/\beta\text{-SiC}$ Whisker Composites

Si_3N_4 can be reinforced with $\beta\text{-SiC}$ whiskers to produce a composite with improved strength at high temperatures and better toughness at low temperatures. In the present case VLS whiskers were used and MgO was added to aid sintering at 1750°C. An amorphous grain boundary phase is frequently observed in Si_3N_4 ceramics /12/ but was not observed in the present material, either at the Si_3N_4 grain boundaries or at the $\text{Si}_3\text{N}_4/\text{SiC}$ interfaces. Instead the MgO was concentrated at triple point pockets. In the example shown in Fig. 9, the pocket is partially crystallized and the lattice spacings and composition are consistent with MgSiO_3 enstatite. Fig. 9 also illustrates the problem of using HREM to analyze interfaces in randomly oriented composites, namely that it is almost impossible to tilt to an orientation where the electron beam is parallel to the interface and two prominence zone axes across the interface. The challenge will be to characterize the structure of such interfaces as a function of processing variables and to correlate with the resulting properties.

(f) $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ Thermal Barrier Coatings

The idea of a thermal barrier coatings (TBC) is to raise the operating temperature of, for example, a gas turbine engine by establishing a temperature gradient across the turbine blade to the underlying nickel-base superalloy. $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ is suitable because of its low thermal conductivity and high thermal expansion. A bond coat with a high Al content is always deposited between the superalloy and TBC in order to form a protective Al_2O_3 film at the interface. In the present case the TBC itself ($\text{ZrO}_2 - 20\text{wt.}\% \text{Y}_2\text{O}_3$) was deposited by electron beam physical vapor deposition (EB-PVD). Cross-sectional TEM specimens were made by sandwich techniques involving slicing, dimpling and ion milling /2/. This was particularly difficult if the adhesion between the TBC and bond coat was poor. In the example shown in Fig. 10, there is good adhesion between the $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ and the $\alpha\text{-Al}_2\text{O}_3$ oxide film on the bond coat. Variations in chemical composition and deposition parameters often gave different phase distribution and $\alpha\text{-Al}_2\text{O}_3$ morphology at the interface. The development of the porosity in this region as a result of post heat treatment led to poor adhesion at the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ interface. Interestingly enough, this interface has previously been studied by HREM in composites of ZrO_2 particles in Al_2O_3 ; the interface is incoherent but there are step-like and dislocations-like features at the interface which help accommodate the mismatch /13/.

4 - CONCLUSIONS

Conventional TEM, AEM and HREM are important techniques for characterizing the microstructure and microchemistry of interfaces in ceramics. Cross-sectional TEM specimens are particularly useful. Highly oriented interfaces such as twins, heteroepitaxial layers and strained layer superlattices can be studied in a straightforward manner to yield information about misfit dislocations at the interface and other defects generated by the misfit strain. Unoriented interfaces, such as general grain boundaries and interphase boundaries in composites and coating systems, are much harder to characterize; care must be taken that the boundary and at least one zone axis are parallel to the electron beam for both HREM and AEM.

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Fig.9: HREM image of clean Si_3N_4 grain boundary and partially crystallized triple point pocket (P).

Fig 10 Cross-section through thermal barrier coating showing bond-coat (B), Al_2O_3 film (A), equiaxed zirconia (EZ) and columnar zirconia (CZ)