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Influence of TiO_2 Additives on the Microstructure of In_2O_3 Ceramics

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Abstract: Titania additives favour densification and hinder grain growth in indium oxide ceramics. The influence of TiO_2 has been investigated, using specimens made by stacking two layers against each other, one of In_2O_3 and the other of $(TiO_2)_x$–$(In_2O_3)_{1-x}$. After sintering, the sharp interface is replaced by a diffuse one, with a graded concentration of TiO_2. Both porosity and grain size decrease when the TiO_2 content increases.

1 INTRODUCTION

Transparent, electrically conductive films of indium–tin oxide (ITO) are used in electro-optical devices that need transparent electrodes.[1] ITO films are mainly processed by DC-magnetron sputtering of ITO targets. Dense targets exhibit better characteristics and lead to better films than porous targets[2] but, unfortunately, In_2O_3-based ceramics do not sinter easily.[3] TiO_2 additives greatly improve densification, as reported by Nadaud *et al.*:[4] for a sintering treatment of 3 h at 1400°C, TiO_2-free ITO densifies to 90% of the theoretical density, whereas 0.5 wt% TiO_2–ITO densifies to nearly 100%. Moreover, TiO_2 reduces the grain growth.

Previous data were related to ITO, whereas the present paper concerns indium oxide. To visualize the influence of TiO_2 additives, the study was carried out using specimens with a graded composition of TiO_2.

2 EXPERIMENTAL PROCEDURE

The starting powder was 99.99 wt% pure In_2O_3 (Metaleurop Recherche, France). It was ultrasonically dispersed in absolute ethanol and dried under vacuum. Then, TiO_2 was added using an alkoxide precursor (titanium butoxide: $Ti[O(CH_2)_3CH_3]_4$). Hydrolytic polycondensation of the titanium butoxide was carried out by adding deionized water, with an excess molar ratio water/alkoxide. The powder mixture was ultrasonically stirred, then dried under vacuum.

Green compacts were pressed to cylindrical pellets (13 mm in diameter and 4 mm in height). The compaction behaviour of the powders was improved by adding a binder (3 wt% of polyvinylbutyral dissolved in hot ethanol) and a plasticizer (0.5 wt% of dibutyl phthalate). Certain pellets were made by stacking two layers of similar thickness (2 mm) against each other. The first layer was TiO_2-free In_2O_3 and the second layer was 2 wt% TiO_2–In_2O_3. The TiO_2-free layer was pressed under 50 MPa, then it was put on to the TiO_2-containing powder bed, and finally the whole assembly was pressed under 150 MPa. A thin platinum wire was put along the interface to help us to locate it in sintered specimens.

Sintering was conducted at temperatures ranging from 1450 to 1550°C, in air, using an $MoSi_2$-heating element electric oven. Microstructures of polished, thermally-etched samples (etching at 220°C below the sintering temperature, for 30 min) were examined by SEM (Jeol 5200, Japan), using SE or BSE modes. Determination of the TiO_2 content and mapping of the Ti-rich segregations were carried out by EDX (Link Pentafet, UK). Grain size was quantified using the linear-intercept method of Wurst and Nelson.[5]

3 RESULTS AND DISCUSSION

3.1 Influence of TiO_2 on densification

Figure 1 shows the shrinkrage of In_2O_3-based ceramics with 0 or 0.5 wt% TiO_2 versus temperature, for a heating treatment at a constant rate ($5°C \cdot min^{-1}$). TiO_2-free materials densify poorly and their residual porosity after treatment at 1550°C is about 20%. In contrast, materials with 0.5% or more of TiO_2 sinter to nearly full density. The shrinkage rate peaks at about 1380°C for TiO_2-free materials and at about 1290°C for TiO_2-containing materials.

3.2 Influence of TiO_2 on grain growth

Exaggerated grain growth generally leads to a separation of pores from grain boundaries, which results in poor densification. Exaggerated grain growth was observed in TiO_2-free materials sintered at 1450°C for times superior to 3 h. Figure 2 shows a duplex microstructure, with both very fine (< 3 μm) and very large (> 50 μm) grains. Temperatures superior to 1450°C or times superior to 3 h lead to monomodal microstructures, with large grains only.

Figure 3 is a schematic diagram and Fig. 4 is an SEM micrograph of the interfacial zone in a two-layer specimen, sintered at 1550°C for 10 h. Visual observations show that the TiO_2-free layer is light yellow, whereas the 2 wt% TiO_2-containing layer is black. Diffusion has allowed the initially sharp interface to transform to a diffuse interface (≈ 100 μm wide), with a graded concentration of titanium. Consequently, there is a continuous change in grain size and porosity, which is associated with the graded content in TiO_2 (Fig. 5). The

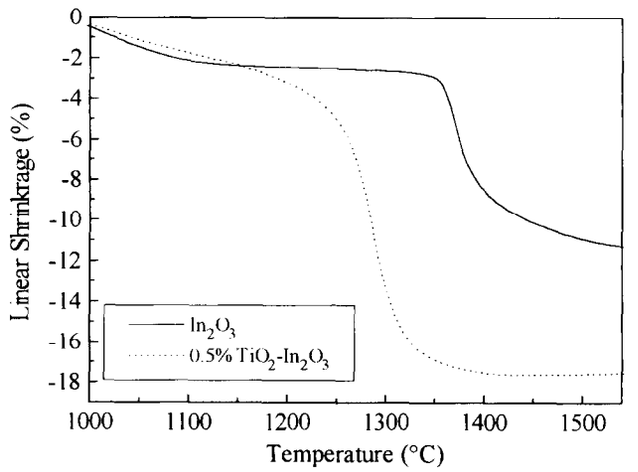

Fig. 1. Shrinkage of x% TiO_2–In_2O_3 ($x = 0$ and 0.5%) vs temperature (heating rate: $5°C \cdot min^{-1}$).

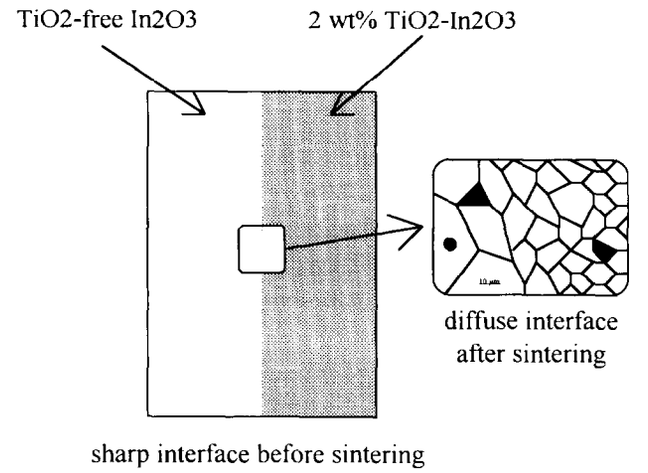

Fig. 3. Schematic diagram of the Ti-rich / Ti-free In_2O_3 interface.

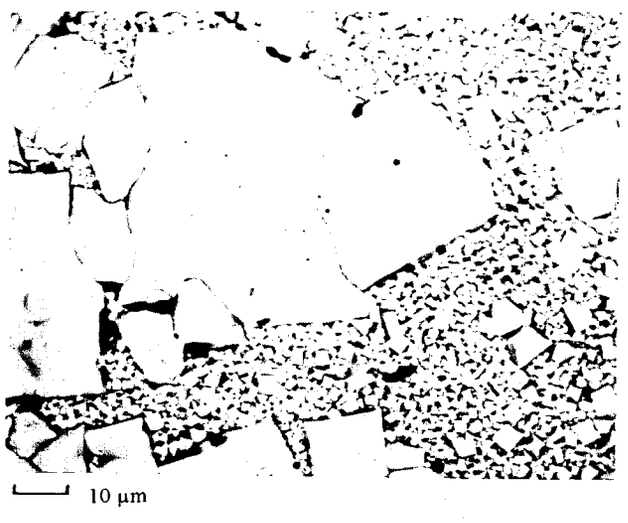

Fig. 2. SEM micrograph of Ti-free In_2O_3 ceramics sintered at 1450°C for 3 h.

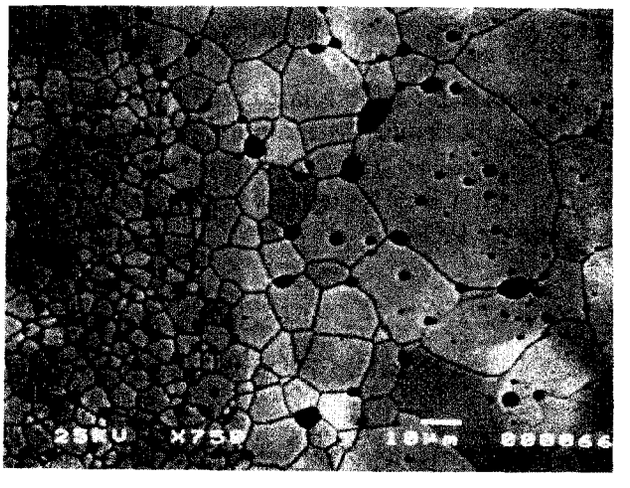

Fig. 4. SEM micrographs of Ti-free/Ti-containing In_2O_3 ceramics sintered at 1550°C for 10 h. Pores appear as black; In_2TiO_5 segregations appear as grey pockets located in tri-grain corners.

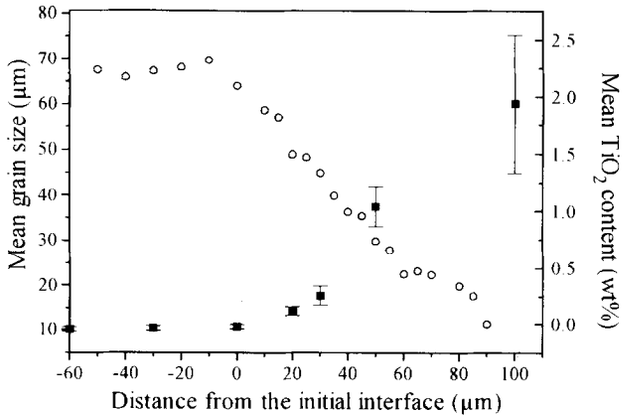

Fig. 5. Mean grain size ((■), measured as indicated in Ref. 5) and mean TiO_2 content ((○) averaged by EDX on 40 μm × 40 μm areas) within the interface zone.

TiO_2-free zone has coarse grains (≈60 μm) with entrapped, round pores and sometimes large voids, whereas the TiO_2-containing zone has uniform, fine grains (≈10 μm), with some intergranular porosity. The solubility limit of TiO_2 in In_2O_3 is about 0.3% and, therefore, there is a precipitation of a TiO_2-rich phase (In_2TiO_5, as characterized by X-ray powder diffraction) when the TiO_2 concentration exceeds this limit. In_2TiO_5 precipitates are segregated in the form of pockets, located in tri-grain corners (Fig. 4).

The present results can be compared to those of Bagley and Lynn Jonhson,[6] who have reported a grain-size gradient in MgO-containing alumina, due to the volatilization of MgO in the superficial zone of specimens. They have concluded that magnesium in solid solution at grain boundaries controls grain growth without the presence of spinel precipitates. The present results are similar, with a progressive decrease in grain size associated with a progressive increase in Ti concentration, down to a constant, minimum grain size as soon as the second phase develops.

4 CONCLUSIONS

The use of a two-layer specimen has allowed us to visualize the beneficial role of TiO_2 additive in In_2O_3 ceramics to increase densification, reduce normal grain growth, and hinder abnormal grain growth. TiO_2 acts at low concentration (< 1%), and its effect saturates when a Ti-rich second phase begins to precipitate.

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REFERENCES

1. VOSSEN, J. L., Transparent conducting films. *Phys.Thin Films*, **9** (1977) 1–71.
2. GEHMAN, B. L., JONSSON, S., RUDOLPH, T., SCHERER, M., WEIGERT, M. & WERNER, R., Influence of manufacturing process of indium tin oxide sputtering targets on sputtering behavior. *Thin Solid Films*, **220** (1992) 333–6.
3. DE WIT, J. H. W., Grain growth and sintering of In_2O_3. *Sci. Ceram.*, **9** (1977) 143–50.
4. NADAUD, N., NANOT, M. & BOCH, PH., Sintering and electrical properties of titania- and zirconia-containing In_2O_3–SnO_2 (ITO) ceramics. *J. Am. Ceram. Soc.*, **77**(3) (1994) 843–6.
5. WURST, J. C. & NELSON, J. A., Lineal intercept technique for measuring grain size in two-phase polycrystalline ceramics. *J. Am. Ceram. Soc.*, **55**(2) (1972) 109.
6. BAGLEY, R. D. & LYNN JONHSON, D., Effect of magnesia on grain growth in alumina. In *Structure and Properties of MgO and Al_2O_3 Ceramics, Advances in Ceramics, Vol. 10*, ed. W. D. Kingery. The American Ceramic Society, Inc., 1984, pp. 666–79.