

Titania as a Sintering Additive in Indium Oxide Ceramics

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The influence of TiO₂ additives on the sintering behavior of In₂O₃ ceramics has been investigated. TiO₂ increases the densification rate, decreases the grain growth during the intermediate stage of sintering, and hinders the pore/boundary breakaway that can affect the final stage of sintering. For a given grain size, TiO₂ shifts the grain size/density trajectory toward higher densities. TiO₂ mainly acts by a second-phase mechanism, but it also may decrease the decomposition rate of In₂O₃.

I. Introduction

TRANSPARENT and conductive thin films made of indium tin oxide (ITO) are used in electronic and optoelectronic applications.¹ Direct-current magnetron sputtering of sintered ITO targets is a common route for making ITO films. The quality of the film is better when the target is dense,² and, moreover, dense targets better resist sputtering erosion. In particular, the surfaces of ion-eroded targets are degraded by conical protrusions ("black spots" or "nodules"),³ whose number decreases when the target porosity decreases. Unfortunately, ITO ceramics do not densify easily.⁴ We have previously⁵ established the following.

(i) The typical density of ITO ceramics sintered at 1400°C for 3 h is only 90%. The microstructure is affected by small pores and large voids.

(ii) ITO vaporizes during heat treatments when non-oxidizing atmospheres are used.

(iii) TiO₂ is an efficient sintering additive. For instance, 0.5 wt% TiO₂-ITO ceramics densify to nearly theoretical density (TD) after a treatment at 1400°C for 3 h.

The influence of TiO₂ on the densification and grain growth of oxides such as Al₂O₃⁶ or Y₂O₃⁷ already has been investigated. Bagley *et al.*⁶ report that the sintering rate of Al₂O₃ gradually increases during the first stage of sintering when the TiO₂ content exceeds a value that is supposed to be the solubility limit (0.1 at.% at 1405°C). They assume that the densification of TiO₂-containing Al₂O₃ is controlled by grain-boundary diffusion in coarse-grained (>2 μm) materials and volume diffusion in fine-grained (<1 μm) materials. Diffusion parameters increase according to a logarithmic law as the TiO₂ content increases. Brook⁸ postulates that vacancies (V_{Al}''') are responsible for enhanced diffusion in TiO₂-doped Al₂O₃. The addition of TiO₂ also increases the activation energy for boundary diffusion.⁹ Gasnier⁷ observes that the influence of TiO₂ in Y₂O₃ is similar to that of MgO in Al₂O₃ and considers that TiO₂ favors densification by preventing the grain-size/density trajectory from crossing the pore/grain-boundary breakaway zone.

Information on the sintering behavior of In₂O₃ is required for a better understanding of the sintering behavior of ITO, and,

therefore, the purpose of the present study is to investigate the role of TiO₂ as sintering additive in In₂O₃ ceramics.

II. Experimental Procedure

Starting powders were fine-grained (0.2 μm mean particle size and 1–3 μm mean agglomerate size), high-purity (99.99 wt%) In₂O₃ (Metaleurop Recherche, Trappes, France). The powders were ultrasonically dispersed in ethanol mixed with 0.8 wt% of a deflocculating agent. TiO₂ was added as a solution of titanium butoxide (Ti(O(CH₂)₃CH₃)₄, 99 wt% pure) previously dissolved in absolute ethanol. Hydrolytic polycondensation of the titanium butoxide was obtained by adding deionized water. In the remainder of the text, the materials doped with titanium are named TiO₂-In₂O₃ and the titanium content is expressed as equivalent TiO₂. After they were stirred ultrasonically, the TiO₂-In₂O₃ powders were mixed with a binder (3 wt% of poly(vinyl butyral) dissolved in hot ethanol) and a plasticizer (0.5 wt% of dibutyl phthalate), vacuum dried, and pressed to pellets (8 mm in diameter and 3–8 mm in height) under a pressure of 150 MPa. The green density of the pellets was ~56% of TD.

Sintering was conducted at temperatures ranging from 1300° to 1550°C, in air, using an electric oven with MoSi₂ heating elements. Isothermal experiments were conducted by rapidly introducing a preheated (600°C for 10 min) specimen into the hot zone of the oven and heating it for various soaking times. Heating rates were very fast in comparison to those used for constant-heating-rate experiments. Dilatometry experiments were conducted in air, with heating rates ranging from 0.8° to 20°C·min⁻¹. The apparent density of the sintered ceramics was measured by the Archimedes method in water. The density of In₂O₃ was taken as 7.15 g·cm⁻³, and true densities of the TiO₂-In₂O₃ materials were derived from a rule of mixtures, assuming that the solubility of TiO₂ in In₂O₃ was very low, as confirmed by various experiments, in particular X-ray diffractometry (XRD), which showed that the lattice parameters of the TiO₂-In₂O₃ did not vary when the TiO₂ content varied. Microstructural observations were conducted by scanning electron microscopy (SEM; scattered electron and backscattered electron (BSE) modes) on polished and thermally etched samples, and they sometimes were conducted by transmission electron microscopy (TEM). Grain size was estimated using the linear-intercept method of Wurst and Nelson,¹⁰ with a correction for the effect of porosity in the ceramics having a relative density <97%. Polystyrene spheres were used as calibrating marks to determine the grain size accurately, and the statistics were always established on ≥300 grains. Quantitative analysis of second-phase precipitates was done by energy-dispersive X-ray analysis (EDX).

III. Results and Discussion

Figure 1 shows the relative density of TiO₂-In₂O₃ ceramics versus sintering time, for various temperatures. Each dot corresponds to an independent sample treated as described above for isothermal experiments. TiO₂ greatly favors densification. After sintering at 1400°C for 10 min, TiO₂-In₂O₃ materials densify to

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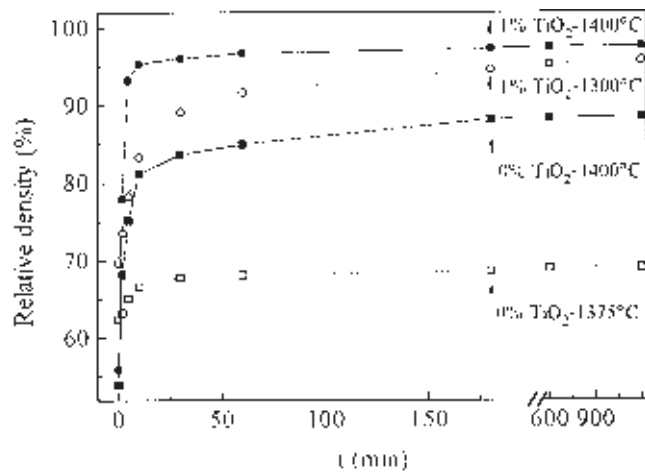


Fig. 1. Relative density versus sintering time for $x\text{TiO}_2\text{-In}_2\text{O}_3$ ceramics ($x = 0$ and 1 wt%) at various temperatures.

95% of TD, whereas untreated In_2O_3 reaches only 82% of TD; the density of 1% $\text{TiO}_2\text{-In}_2\text{O}_3$ is 98% of TD after 1 h of sintering, whereas the density of untreated In_2O_3 is 88% of TD after 10 h.

Figure 2 shows the grain size/densification trajectories for In_2O_3 and 1% $\text{TiO}_2\text{-In}_2\text{O}_3$ sintered at 1400°C. Grain growth develops at early densification (80% of TD) in In_2O_3 and at much higher densification (93% of TD) in 1% $\text{TiO}_2\text{-In}_2\text{O}_3$. The beginning of grain growth in 1% $\text{TiO}_2\text{-In}_2\text{O}_3$ seems to correspond to the closure of porosity, which is estimated¹¹ to occur at ~91% of TD in a model with tetrakaidecahedron grains. There is usually a competition between densification and grain growth during the intermediate stage of sintering, and, therefore, one would believe that the beneficial influence of TiO_2 on densification is related to the flattening of the grain size/densification trajectory.

For sintering times >10 h (at 1400°C), In_2O_3 ceramics are affected by abnormal grain growth. Coarse grains (20–30 μm) progressively develop at the expense of normal grains, until the microstructure is entirely composed of such large grains for sintering times >50 h. However, the porosity does not change noticeably during the abnormal grain-growth process (see Fig. 2). In 1% $\text{TiO}_2\text{-In}_2\text{O}_3$, the negligible grain growth during the intermediate stage of sintering prevents the trajectory from crossing the pore/grain breakaway zone^{12,13} after porosity closure.

Figures 3(A) and (B) show micrographs of In_2O_3 and 1% $\text{TiO}_2\text{-In}_2\text{O}_3$ sintered at 1400°C for 20 h. The microstructure of

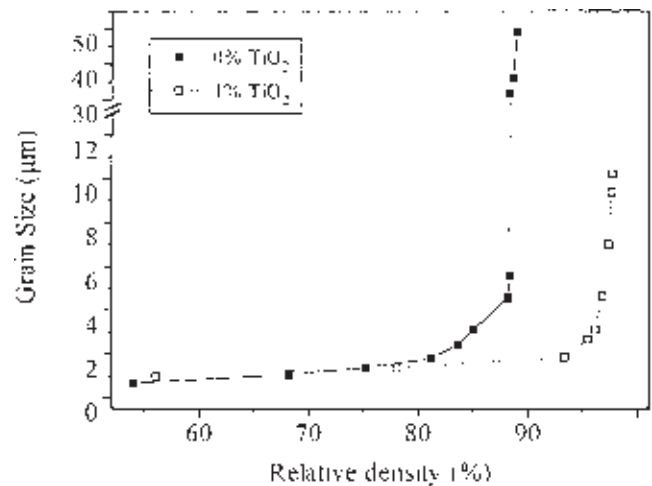


Fig. 2. Grain size versus relative density for $x\text{TiO}_2\text{-In}_2\text{O}_3$ ceramics ($x = 0$ and 1 wt%) sintered at 1400°C.

In_2O_3 is characterized by a bimodal grain-size distribution, with spherical pores entrapped within coarse grains. In contrast, the microstructure of $\text{TiO}_2\text{-In}_2\text{O}_3$ is fine and monomodal, with no pore entrapment. When the TiO_2 content exceeds 0.5 wt%, one observes the presence of dark precipitates, mainly located along grain boundaries and at triple-grain corners. Chemical analysis by EDX shows a phase composition similar to that of In_2TiO_5 , as discussed later.

Figure 4 shows the relative densities of $x\text{TiO}_2\text{-In}_2\text{O}_3$ samples (x from 0 to 2 wt%) versus temperature for heat treatments at constant rate (5°C·min⁻¹). The densification data have been derived from dilatometry experiments. Three comments are pertinent.

(i) $\text{TiO}_2\text{-In}_2\text{O}_3$ ceramics sinter to almost full density when the TiO_2 content is ≥ 0.5 wt%, whereas lower contents are not very effective (for instance, 0.2 wt% of TiO_2 allows a density of only 85%, even if the sintering temperature is increased to 1550°C). On the other hand, adding substantially more than 0.5% of TiO_2 does not substantially increase the densification.

(ii) In_2O_3 doped with ≥ 0.5 wt% TiO_2 can be sintered at low temperatures (~1300°C).

(iii) The presence of TiO_2 decreases the temperature where the densification rate is a maximum. For a heating rate of 5°C·min⁻¹, the densification rates are maximum at 1380°, 1350°, and 1290°C for 0, 0.2, and 1 wt% TiO_2 , respectively.

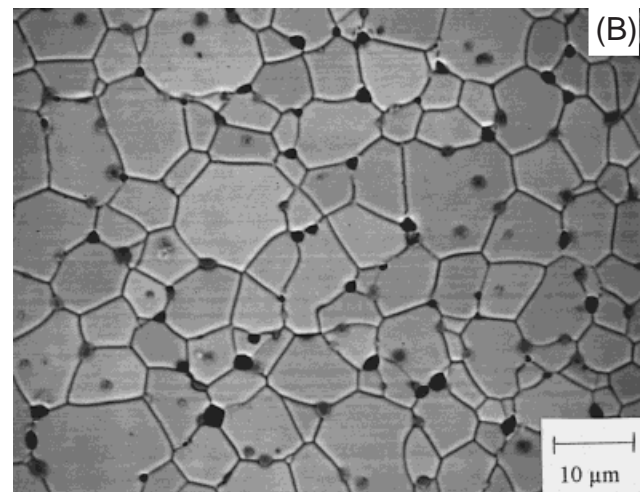
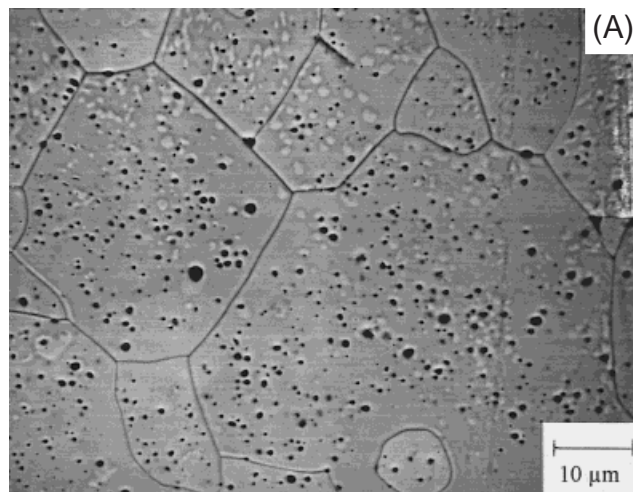


Fig. 3. SEM micrographs (BSE mode) of (A) In_2O_3 and (B) 1% $\text{TiO}_2\text{-In}_2\text{O}_3$ ceramics sintered at 1400°C for 20 h, in air.

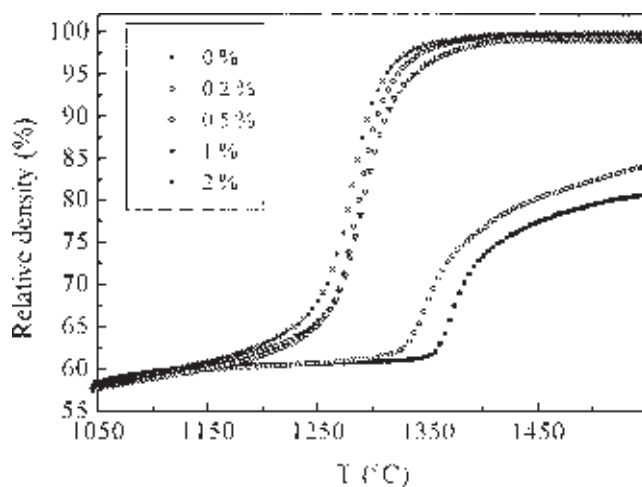


Fig. 4. Relative density versus temperature for $x\text{TiO}_2\text{-In}_2\text{O}_3$ ceramics ($x = 0, 0.2, 0.5, 1$, and 2 wt%) at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$.

Isothermal sintering experiments can be used for estimating the changes in diffusion coefficients and diffusion paths associated with the use of TiO_2 additives. Common sintering models^{14,15} express the densification rate dp/dt as

$$\frac{dp}{dt} = \frac{A_0 D_d}{TG^n} f(\rho) \quad (1)$$

where A_0 is a constant, T the temperature, D_d the thermally activated diffusion coefficient that controls the densification process, G the mean grain size, n the grain-size exponent (which depends on the diffusion mechanism; e.g., $n = 3$ for lattice diffusion and $n = 4$ for grain-boundary diffusion), and $f(\rho)$ a term that is a function of density only and is equal to one when lattice diffusion is the operating mechanism.

Equation (1) indicates that an increase in dp/dt , at a given temperature and for a given mechanism, can be due to either an increase in D_d or a decrease in the grain-growth rate. D_d and n can be determined by plotting $\log dp/dt$ vs $\log G$, as shown in Fig. 5. The values of D_d and n that are derived from the intercepts and slopes of data lines in Fig. 5 are given in Table I. The contribution of $f(\rho)$ is assumed to be noticeable for the very short sintering times only, and, therefore, this contribution is generally neglected. A deviation from linearity is observed for long times, as in MgO -doped Al_2O_3 .¹⁶ In all cases, $n \approx 4$, which suggests a control by grain-boundary diffusion. Table I shows that TiO_2 additions increase D_d by a factor of 6, in materials sintered at 1400°C .

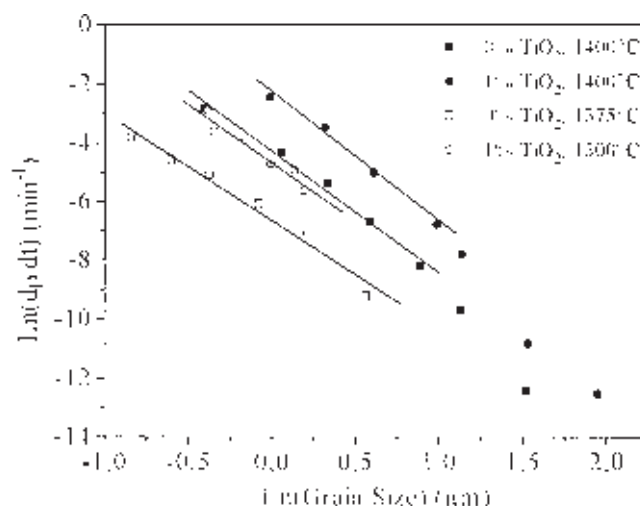


Fig. 5. Logarithm of densification rate versus logarithm of grain size for $x\text{TiO}_2\text{-In}_2\text{O}_3$ ceramics. (x is 0 and 1 wt%).

Table I. Least-Square Fits for Densification Kinetics^a

Parameter	Temperature ($^\circ\text{C}$)/ TiO_2 content (%)			
	1375/0	1400/0	1300/1	1400/1
n	3.88	4.28	3.95	4.40
$\ln A_0 D_d/T$	-6.64	-4.14	-4.66	-2.34
Slope change		1		$\uparrow \times 6$
Regression factor (R)	0.991	0.993	0.970	0.995

^a $dp/dt \approx A_0 D_d/TG^n$; plot: $\ln dp/dt$ vs $\ln G$.

Constant-heating-rate experiments were conducted to determine the influence of TiO_2 on the activation energy of densification, using the method described by Wang and Raj.⁹ For constant heating rates, Eq. (1) becomes

$$\alpha \frac{dp}{dT} = A \frac{\exp(-E_d/RT)}{TG^n} f(\rho) \quad (2)$$

where $\alpha = dT/dt$ is the heating rate, E_d the activation energy, and A a constant independent of T . Taking the logarithm of both sides of the equation, we have

$$\ln \alpha T \frac{dp}{dT} = -\frac{E_d}{RT} + \ln f(\rho) + \ln A - n \ln G \quad (3)$$

E_d can be determined by plotting $\ln \alpha T(dp/dT)$ vs $1/T$ at constant values of ρ and G . Figure 6 shows densification rates versus temperature in materials with 0% and 1% TiO_2 treated at various heating rates (2° , 5° , 10° , and $20^\circ\text{C}\cdot\text{min}^{-1}$). The temperature where the densification rate is a maximum increases with heating rate. Furthermore, final densities for titanium-free materials increase when the heating rate increases, whereas final densities for titanium-containing materials show no heating rate effect. Figure 7 shows Arrhenius plots derived from Eq. (3); each data line corresponds to a given density. To maintain the condition of constant grain size, the relative densities must be selected between 60% and 70% for In_2O_3 and between 70% and 80% for 1% $\text{TiO}_2\text{-In}_2\text{O}_3$. (Figure 2 shows there is no noticeable grain growth in these density domains.) For each relative density, four plots have been obtained using four different heating rates. The apparent activation energy for sintering of In_2O_3 has been found to be $580 \pm 40 \text{ kJ}\cdot\text{mol}^{-1}$ and that of 1% $\text{TiO}_2\text{-In}_2\text{O}_3$ to be $450 \pm 30 \text{ kJ}\cdot\text{mol}^{-1}$. The decrease (of $\sim 20\%$) in the apparent activation energy is believed to be partially responsible for the increase in the diffusion coefficient.

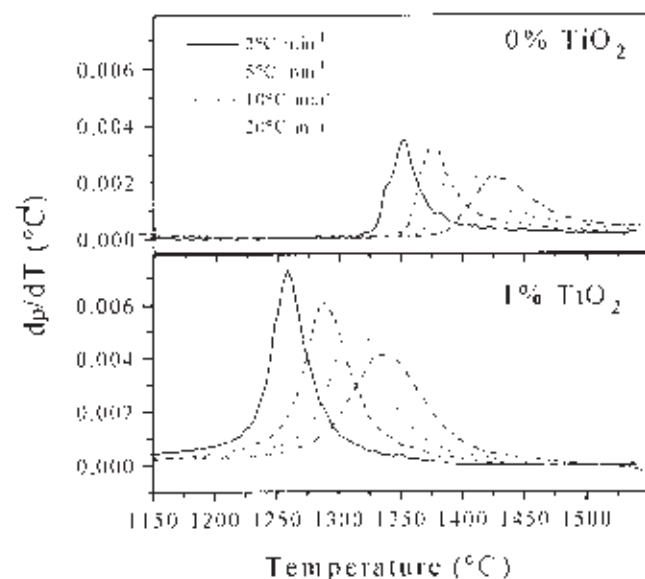


Fig. 6. Derivatives of densification (dp/dT) versus temperature for $x\text{TiO}_2\text{-In}_2\text{O}_3$ ceramics ($x = 0$ and 1 wt%) for sintering experiments at fixed heating rates.

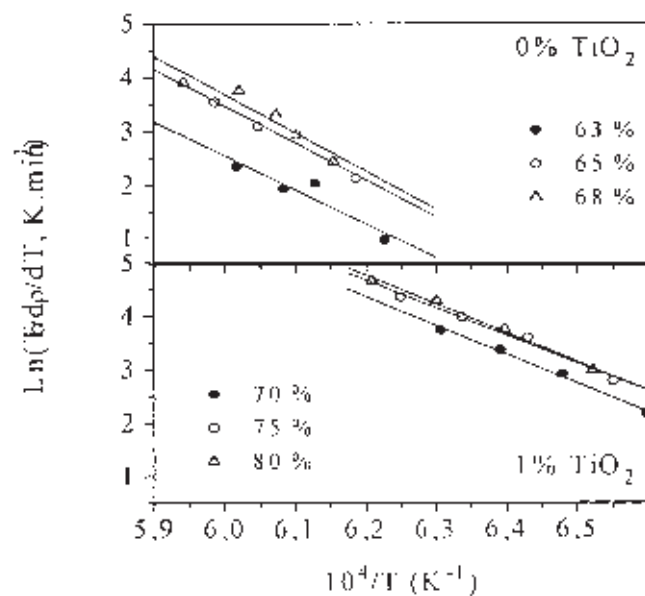


Fig. 7. Arrhenius plots for the densification of $x\text{TiO}_2\text{-In}_2\text{O}_3$ ($x = 0$ and 1 wt%).

To summarize, TiO_2 has an influence as a sintering additive in In_2O_3 ceramics.

(i) TiO_2 strongly increases the densification rate and lowers the densification temperature.

(ii) The critical amount of TiO_2 required to reach full densification is ~ 0.5 wt%.

(iii) TiO_2 inhibits grain growth. In contrast, undoped In_2O_3 exhibits abnormal grain growth, and, therefore, its densification is blocked by pore entrapment.

(iv) The densification process seems to be controlled by grain-boundary diffusion in both In_2O_3 and $\text{TiO}_2\text{-In}_2\text{O}_3$. The presence of TiO_2 decreases the apparent activation energy of densification.

The sudden increase in shrinkage that is observed in $\text{TiO}_2\text{-In}_2\text{O}_3$ ($\text{TiO}_2 \geq 0.5\%$, see Fig. 4) might suggest the presence of a liquid phase, and, therefore, this question has been investigated. However, both thermal analysis and TEM have provided a negative answer. Differential thermal analysis (DTA) experiments (between room temperature and 1450°C) on In_2O_3 to which various amounts of TiO_2 (up to 20%) have been added, show no endothermic peaks. TEM micrographs show that the triple points and grain boundaries (between In_2O_3 and In_2O_3 or between In_2O_3 and precipitates, Figs. 8(A) and (B), respectively) are free of exliquid residue. Moreover, the decrease in activation energy of sintering associated with the addition of TiO_2 does not favor a liquid phase, which generally increases the activation energy by adding a heat-of-solubility term to the initial activation energy.¹⁷ All this means that $\text{TiO}_2\text{-In}_2\text{O}_3$ densifies through solid-state sintering.

Although the influence of TiO_2 in In_2O_3 shows some similarities with that of MgO in Al_2O_3 ,^{16,18} there are at least three differences.

(i) TiO_2 is effective at an early stage of sintering, whereas MgO has been reported to lower densification in the initial stage but to enhance it in the final stage.

(ii) Untreated In_2O_3 exhibits very low densification and can vaporize, whereas undoped Al_2O_3 easily densifies to $>95\%$ of TD and does not vaporize at usual sintering temperatures.

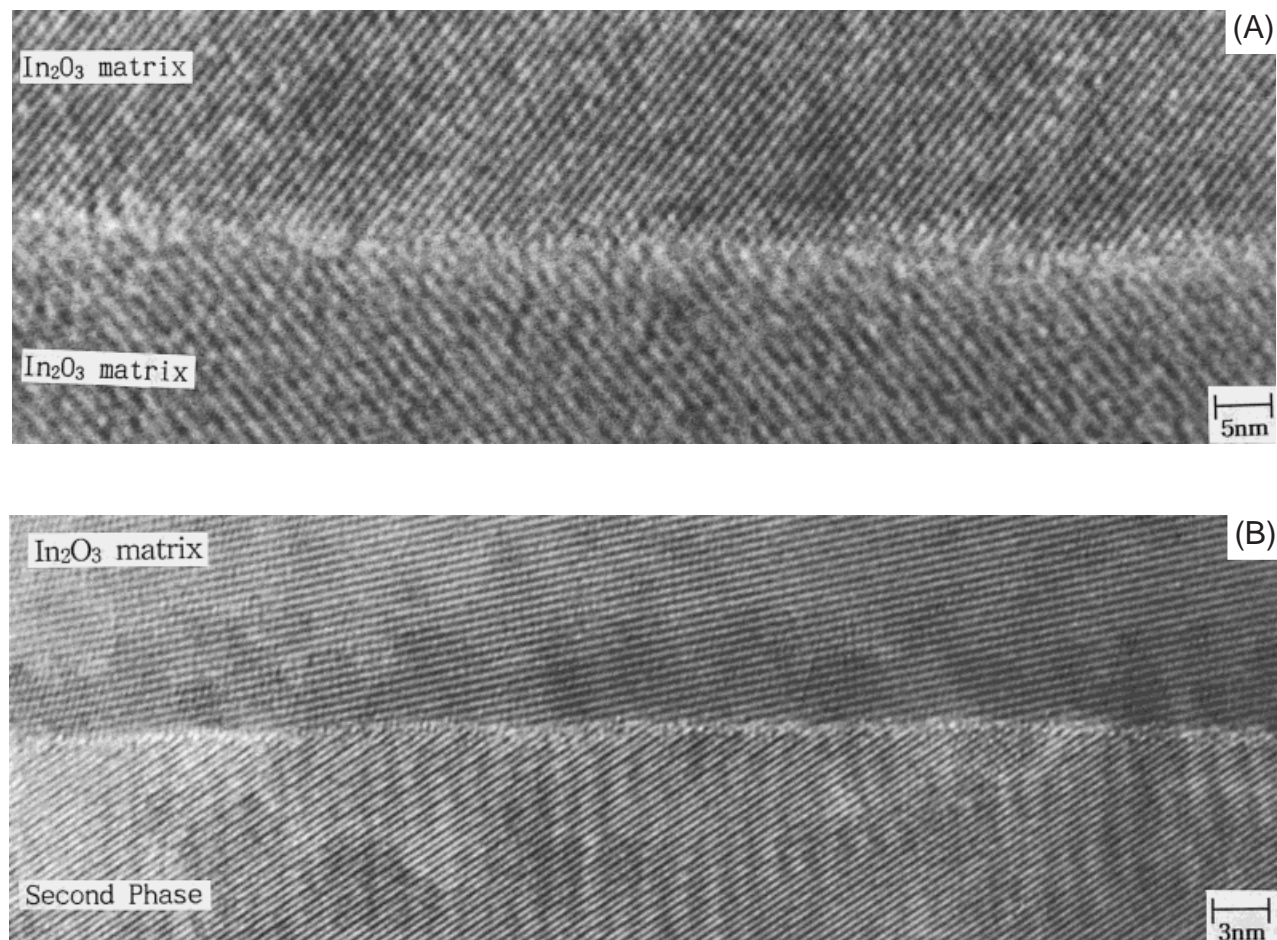


Fig. 8. TEM microstructures of (A) homogeneous grain boundary and (B) heterogeneous grain boundary.

(iii) TiO_2 requires rather noticeable concentrations (>0.5 wt%) to be operative in In_2O_3 , whereas MgO is operative in Al_2O_3 even in very low concentration (<0.025 wt%, i.e., below the solubility limit).

To support the third point, we can note that the existence of second-phase precipitates in TiO_2 - In_2O_3 ceramics begin to be detected when the TiO_2 content exceeds 0.5%, which suggests that the solubility limit of TiO_2 in In_2O_3 is just below 0.5%. Quantitative EDX experiments on precipitates indicate an $\text{In}:(\text{In} + \text{Ti})$ ratio of about 2:3, which corresponds to the stoichiometry of In_2TiO_5 . Moreover, titanium-rich In_2O_3 materials (TiO_2 content ≥ 1 wt%) have XRD patterns that show the presence of In_2TiO_5 peaks. The marked change in the sintering behavior when the TiO_2 content increases from 0.2% to 0.5% corresponds to a change from a single-phase to a two-phase system, as reported by Bagley *et al.*⁶ in TiO_2 -containing Al_2O_3 and Lu and De Jonghe¹⁹ in Nd_2O_3 -containing BaCeO_3 .

Solid-state sintering additives usually act through one or more of three mechanisms: solid-solution effect (diffusion enhancement); solute-segregation effect (segregation in the vicinity of grain boundaries and grain-growth hindrance by solute-drag mechanism); and second-phase effect (grain-boundary pinning).

Substituted to In^{3+} , Ti^{4+} can lead to the formation of indium vacancies ($V_{\text{In}}^{\text{III}}$), which may promote cationic diffusion, as reported for TiO_2 - Al_2O_3 ^{6,8} and TiO_2 - Y_2O_3 .⁷ However, the fact that TiO_2 is not effective below the solubility limit shows that a solid-solution mechanism is not predominant here. In contrast, the In_2TiO_5 precipitates appear to be important, seemingly by pinning the grain boundaries and, therefore, by impeding abnormal grain growth. Moreover, the titanium-enriched grain-boundary zones may provide an easier diffusion path than the "clean" $\text{In}_2\text{O}_3/\text{In}_2\text{O}_3$ boundaries.

In addition to its role to form precipitates, TiO_2 may be effective by decreasing the decomposition rate of In_2O_3 . As previously mentioned, undoped In_2O_3 exhibits the peculiar behavior that grain growth is very precocious: it begins in the intermediate stage of sintering, whereas in most poorly densified ceramics the pinning of grain boundaries by pores is strong enough for limiting grain growth until the porosity has been greatly reduced. In the present case, grain growth can be promoted by an evaporation-condensation mechanism,²⁰ associated with the easy decomposition of In_2O_3 :



The equilibrium partial pressure of In_2O_3 in air has been reported²¹ to be $\sim 10^{-5}$ atm (1 Pa) at 1500°C . We have studied the decomposition of In_2O_3 by weight-loss experiments,⁵ as shown in Fig. 9, where weight loss is plotted versus temperature for In_2O_3 and TiO_2 - In_2O_3 powders. The addition of TiO_2 strongly reduces the decomposition. Moreover, TiO_2 - In_2O_3 ceramics begin to densify at lower temperatures ($<1300^\circ\text{C}$), which decreases the area of solid-vapor interfaces and, therefore, limits the decomposition at high temperatures ($T > 1320^\circ$ to 1350°C), where the decomposition rate becomes fast. Another reason for the beneficial influence of TiO_2 in decreasing decomposition rate is found in Eq. (4): the partial substitution of indium by titanium ($\text{Ti}_{\text{In}}^{\text{III}}$) can be balanced by either cationic vacancies ($V_{\text{In}}^{\text{III}}$) or interstitial oxygens ($\text{O}_{\text{In}}^{\text{II}}$). In the latter case, the equilibrium is displaced in the sense that it limits decomposition.

IV. Conclusions

TiO_2 is effective as a sintering additive in In_2O_3 ceramics. The minimum TiO_2 content that is required to sinter high-density ceramics is 0.5 wt%, which corresponds to the precipitation of In_2TiO_5 . There is no liquid phase. Grain size/density trajectories show that TiO_2 greatly enhances the densification-rate:grain-growth ratio. Three mechanisms can explain the beneficial role of TiO_2 : decreased grain growth by pinning grain

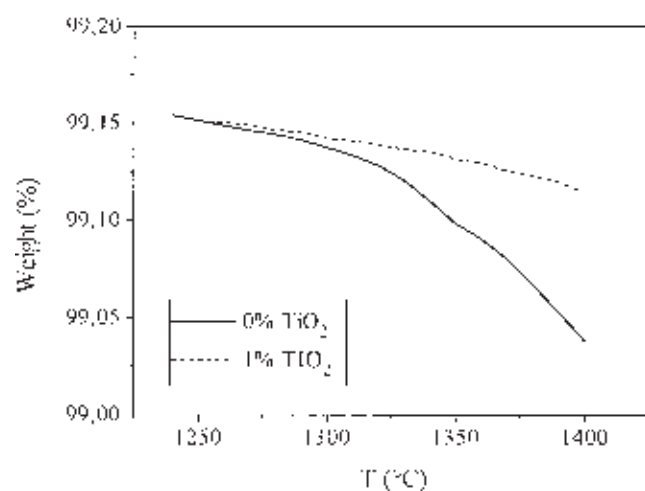


Fig. 9. Thermogravimetric analysis of $x\text{TiO}_2$ - In_2O_3 ($x = 0$ and 1 wt%) heated to 1400°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

boundaries by In_2TiO_5 precipitates (in the final stage of sintering); increased grain-boundary diffusion rate because of a decrease in the corresponding activation energy; and decreased decomposition of In_2O_3 (in the intermediate stage of sintering).

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