

Low temperature synthesis of $Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$ films by sol–gel processing

Plinio Innocenzi^{a,*}, Alessandro Martucci^b, Lidia Armelao^c

^a *Dipartimento di Architettura e Pianificazione, Materials Science and Nanotechnology Laboratory and INSTM, Università di Sassari, Palazzo Pou Salid, Piazza Duomo 6, 07041 Alghero (Sassari), Italy*

^b *Dipartimento di Ingegneria Meccanica, Settore Materiali, Università di Padova, via Marzolo 9, 35131 Padova, Italy*

^c *Dipartimento di Scienze Chimiche, ISTM-CNR and INSTM, Università di Padova, via Marzolo 1, 35131 Padova, Italy*

Received 7 April 2004; received in revised form 31 August 2004; accepted 12 September 2004

Available online 22 December 2004

Abstract

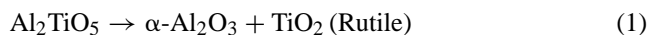
Aluminium titanate films thicker than 0.5 μm have been synthesized by sol–gel methods. The films have been deposited via repetitive dip-coating on silicon wafers and their thermal stability has been tested as a function of the annealing time and temperature. The sol–gel approach has allowed the formation of the aluminium titanate phase at temperatures ($\sim 700^\circ\text{C}$) much lower than those necessary for solid-state reactions ($\sim 1450^\circ\text{C}$). Magnesium oxide has been used to improve the thermal stability of the films at high temperatures. The behavior of samples prepared with two different Mg content, i.e. $Mg_{0.2}Al_{1.6}Ti_{0.8}O_5$ and $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$, has been studied. The films have proven to be stable at 1150°C , for up to 90 h. X-ray photoelectron spectroscopy has shown that after firing at 500°C the surface chemical composition of the films is in accordance with the nominal one, whilst at higher annealing temperatures some differences, attributed to diffusion effects, have been observed.

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Keywords: Films; Al_2TiO_5 ; Sol–gel processes; X-ray methods

1. Introduction

Aluminium titanate materials show several interesting properties,¹ such as a low thermal expansion coefficient, low thermal conductivity and a very high thermal shock resistance that suggest the use of these ceramics in many different applications. The easy tendency to decompose following the reaction:²



represents, however, a serious limitation to a widespread utilization of aluminium titanate based materials.

The formation of aluminium titanate is generally obtained through a solid-state reaction between crystalline rutile TiO_2 and $\alpha-Al_2O_3$. Aluminium titanate exists in two allotropic

forms, α and β , and the phase diagram shows an eutectoid temperature at 1280°C . The low-temperature phase, $\beta-Al_2TiO_5$, has two temperature ranges of stability, the first from room temperature up to around 750°C , and the second from 1280°C up to the inversion temperature at 1820°C . The high-temperature phase, $\alpha-Al_2TiO_5$, is stable from 1820°C up to the melting temperature, 1860°C . Below 1280°C , aluminium titanate decomposes, into $\alpha-Al_2O_3$ and rutile titania (Eq. (1)). The decomposition process is very slow below 900°C , whilst in the range 900 – 1200°C it accelerates with a maximum decomposition rate at 1100 – 1150°C , a range in which full decomposition is observed after annealing from 5 to 50 h.

A great part of the recent research has been, therefore, devoted to the basic understanding of the decomposition mechanisms^{3,4} and to increase the overall thermal stability. Interesting improvements have been obtained by the addition of MgO or Fe_2O_3 during the sintering process,^{5,6} whilst

* Corresponding author. Tel.: +39 079 9720408; fax: +39 079 9720420.
E-mail address: plinio@uniss.it (P. Innocenzi).

Table 1

Amounts of the different components used to obtain oxides of composition $Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$, with the selected values of x in the first column

x	EtOH (cc)	HNO ₃ (cc)	Acac (cc)	MgCl ₂ (g)	Al(O- <i>s</i> -Bu) ₃ (cc)	Ti(OBu) ₄ (cc)
0	40	0.03	0	0	1	0.66
0.2	40	0.02	0.38	0.05	0.5	0.5
0.6	40	0.04	0.75	0.3	0.5	1.3

other oxides such as ZrO₂ and SiO₂ have not been shown to increase the thermal stability. More recently, the addition of alkali feldspar, has been proposed as another way to enhance the mechanical and thermal resistance of aluminium titanate.⁷ All these preparations are based on a solid state reaction of alumina and titania, with the eventual presence of the stabilizing oxide, at temperatures higher than the eutectoid one (1280 °C).

Sol-gel processing represents an interesting alternative. One advantage is the higher purity of the components that will reduce the rate of thermal decomposition, which has been shown to be largely related to the presence of impurities in the precursor materials.⁴ Another very interesting feature is represented by the possibility to synthesize aluminium titanate at “low temperature”.⁸ Direct formation of aluminium titanate can be achieved at temperatures around 600 °C via non-hydrolytic synthesis^{9,10} and around 800 °C by a synthesis with alkoxides stabilized with acetylacetonate.¹¹ The formation of β -Al₂TiO₅ at low temperatures is attributed to a diffusion-limited crystallization process, which takes place in conditions of high homogeneity at the molecular level reached in the material thanks to sol-gel processing.^{12,13}

The present authors have successfully extended the low temperature sol-gel synthesis to the preparation of aluminium titanate films.^{14,15} The possibility to fabricate β -Al₂TiO₅ films opens, in fact, interesting perspectives in different fields of technological interest. Whilst, in fact, the literature on powder and bulk β -Al₂TiO₅ materials and their stabilization at high temperature is quite extended, very few reports have appeared on films. The fabrication of aluminium titanate thick and crack-free films is, in fact, a difficult task and sol-gel processing appears to be a possible feasible route. It should be emphasized, however, that even using a sol-gel route, a specific synthesis, because of the structural difference between sol-gel powders and films, must be employed to fabricate and stabilize β -Al₂TiO₅ films.

The main goal, also in the case of aluminium titanate films, is to reach a long thermal stability to enhance the protective effects. In the present paper we extend our previous work to aluminium titanate films stabilized with magnesia that is expected to hinder the thermal decomposition.

2. Experimental

Aluminium tri-*sec*-butoxide (Al(O-*s*-Bu)₃), titanium tetrabutoxide (Ti(OBu)₄), and dichloromagnesium hexahydrate (MgCl₂·6H₂O) were used as precursors for the oxide

components. They were all purchased from Aldrich, reagent grade and used without further purification. 2,4-Pentanedione (acac) (Aldrich), nitric acid (HNO₃) (Prolabo), 1N, and absolute ethanol (Carlo Erba) were used as-received.

To prepare the films of composition Al₂TiO₅ (undoped aluminium titanate) Al(O-*s*-Bu)₃ was carefully added to refluxing EtOH (80 °C) and immediately after Ti(OBu)₄ was slowly added under magnetic stirring. The sol was cooled to room temperature, and then HNO₃ (1N) was added, the resulting sol was stirred for 1 h and used fresh for dip-coating. The protocol to prepare aluminium titanate containing magnesia was modified as follows.

After the addition of Al(O-*s*-Bu)₃ in EtOH and Ti(OBu)₄, acac was introduced followed by MgCl₂·6H₂O in EtOH. HNO₃ was finally added to catalyze the sol. The amounts of components employed for the preparation of the sols are listed in Table 1. The preparation protocol is shown in Fig. 1.

Films were deposited from fresh sols by dip-coating in a humidity-controlled box, with a relative humidity lower than 30%. Silicon wafers were used as substrates. A repetitive dip-coating was used to deposit up to five layers with 1.85 cm s⁻¹ of withdrawal rate. After each deposition the films were stabilized with a firing step at 500 °C for 1 h in air. The multilayer samples were put directly in the preheated furnace and fired in air at temperatures between 600 and 1200 °C with a step of 100 °C. The coating thickness was measured with a pro-

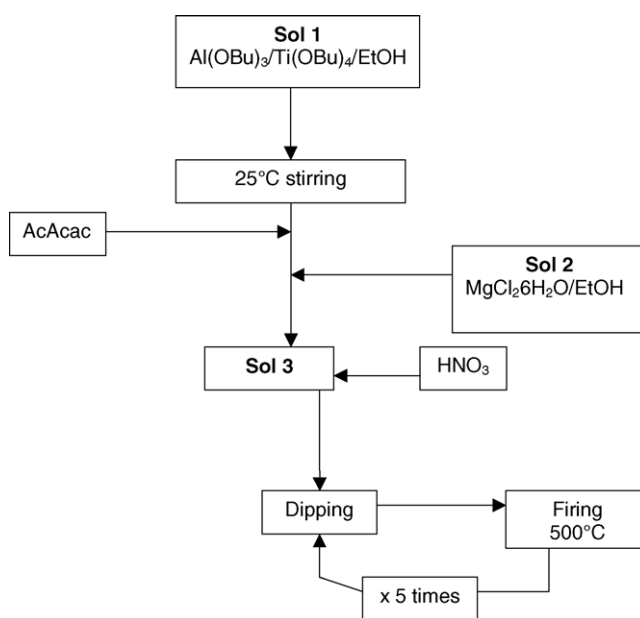


Fig. 1. Flow chart of the $Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$ precursor sols synthesis.

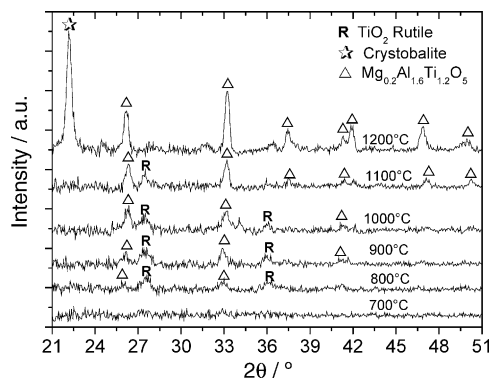


Fig. 2. XRD patterns of $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{0.8}\text{O}_5$ films annealed at different temperatures.

filometer. Thicknesses of about 100–200 nm per single layer were obtained.

X-ray diffraction analysis (XRD) was performed on the films using a diffractometer with a glancing angle configuration for thin film samples. $\text{Cu K}\alpha$, operating at 40 kV and 50 mA, was used as the radiation source (one scan, 5 s acquisition time, $2\theta^\circ$ angle from 15° to 70° and a fixed glancing angle $\theta = 0.5^\circ$). The average crystallite size was calculated from the Scherrer equation after the experimental patterns were fitted using the method described by Enzo et al.¹⁶

The surface chemical composition of the films was investigated by X-ray photoelectron spectroscopy (XPS). The analysis was performed on a Perkin-Elmer Φ 5600-ci spectrometer using monochromatized $\text{Al K}\alpha$ radiation (1486.6 eV). The working pressure was $<5 \times 10^{-8}$ Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the $\text{Au } 4f_{7/2}$ line at 83.9 eV with respect to the Fermi level. The standard deviation for the BE values was 0.15 eV. Wide scans (survey) were obtained in the BE range 0–1350 eV. Detailed scans were recorded for the $\text{Al}2p$, $\text{Al}2s$, $\text{Ti}2p$, $\text{Ti}3p$, $\text{O}1s$, OKLL , $\text{C}1s$, $\text{Mg}1s$, $\text{Mg}2s$, $\text{Mg}2p$, MgKLL and $\text{Si}2p$ regions. As an internal reference for the peak positions, the $\text{C}1s$ peak of adventitious carbon was assumed at 284.8 eV.¹⁷ The atomic compositions were evaluated using sensitivity factors supplied by Φ V5.4A software. The samples were introduced directly, by a fast entry lock system, into the XPS analytical chamber.

3. Results and discussion

The formation of the magnesia stabilized aluminium titanate phase (JCPDS 87-0920) in the films prepared from the precursor sol whose theoretical composition was $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{1.2}\text{O}_5$, started after firing at 800°C (Fig. 2). Higher annealing temperatures produced an increase in intensity of $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{1.2}\text{O}_5$ diffraction peaks.

The presence of rutile titania (JCPDS 87-0920) from 800°C was also detected, however, the diffraction peaks assigned to this phase did not increase in intensity with the firing temperature and, at 1200°C , the phase was no longer

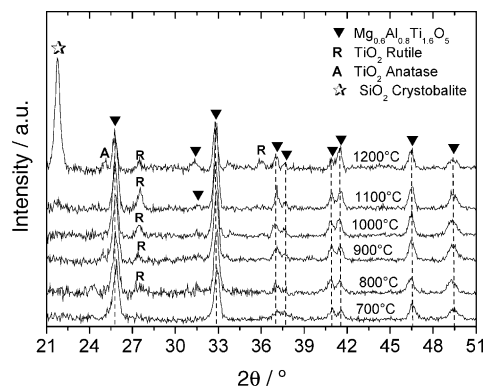


Fig. 3. XRD patterns of $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ films annealed at different temperatures.

observed. The diffraction patterns also show that titania crystallized directly to rutile without transformation from the anatase phase. In addition, at 1200°C an intense diffraction peak at 22.1° , assigned to silica cristobalite (JCPDS 82-1409) and grown from the silicon substrate, was observed, whilst the $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{1.2}\text{O}_5$ phase did not decompose even after firing at 1100 and 1200°C .

A similar trend was observed in $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ films after firing from 700 up to 1200°C (Fig. 3). $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ showed a good stability up to 1200°C and titania rutile was observed from 800°C . In these samples the magnesia aluminium titanate phase formed at even lower temperatures, in fact, at 700°C the diffraction peaks assigned to $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ are already well detected. Titania anatase (JCPDS 84-1285) was observed to form from 1100°C , similarly to our previous observations in $\beta\text{-Al}_2\text{TiO}_5$ films.¹⁴ At 1200°C silica cristobalite from the substrate was also observed.

The formation of titania rutile and anatase observed in the two set of samples $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{1.2}\text{O}_5$ and $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$, does not derive from the thermal decomposition of the magnesia aluminium titanate phases but we assume that it is formed directly from residual amorphous titania. The presence of titania is accompanied by an increase in the crystallite sizes and intensity of the diffraction peaks of $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{1.2}\text{O}_5$ and $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ with the annealing temperature. It is interesting to observe that, with respect to the low temperature sol-gel preparation of $\beta\text{-Al}_2\text{TiO}_5$ films,^{14,15} the introduction of the third component in the precursor sol during the synthesis is not disrupting the local order that allows the formation of the aluminium titanate phases.

Fig. 4 shows the changes of the crystallite sizes (33°) in $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{1.2}\text{O}_5$ and $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ as a function of the thermal treatment. A constant increase in the crystallite size is observed with the increase of the temperature in both samples.

An important property that should be tested in aluminium titanate materials is the endurance to thermal decomposition. As shown by Buscaglia and Nanni^{3,4} the decomposition rate has a maximum in the range $1100\text{--}1150^\circ\text{C}$, we have therefore

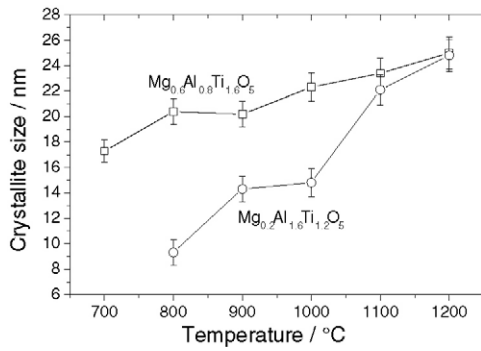


Fig. 4. Crystallite size variations of $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ and $\text{Mg}_{0.2}\text{Al}_{1.6}\text{Ti}_{0.8}\text{O}_5$ as a function of the thermal treatment temperature.

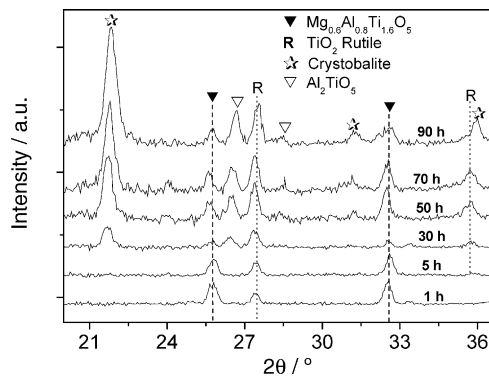


Fig. 5. XRD patterns of $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ films as a function of the annealing time at 1150°C .

tested the behavior of the samples at 1150°C for different annealing times.

Fig. 5 shows the diffraction patterns of $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ films after firing at increasing times, up to 90 h. Silica cristobalite from the oxidation of the substrate was observed under heating between 5 and 30 h. The $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ phase

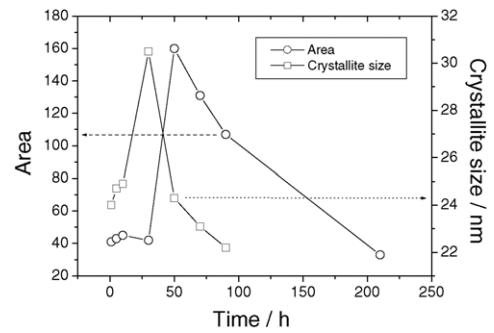


Fig. 6. Changes of the crystallite dimensions and area of the diffraction peak at 33° in $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ films at different annealing times.

did not completely decompose even after the longest thermal treatment at 90 h. The area and crystallite sizes (33°) of $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ (Fig. 6) show that after a steady increase up to 30 h of firing, an abrupt decrease is observed in the following 30 h.

This is an indication of $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ decomposition in the films. However, at longer annealing times, new diffraction peaks are observed at 26.5° and 33.7° , which are attributed to the formation of a pure aluminium titanate phase (JCPDS 73-1630).

The direct observation of the surface by scanning electron microscopy (SEM) has evidenced the presence of microcracks in the surface at higher temperatures of firing. Fig. 7 shows the SEM pictures of a $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ film after annealing at 1100°C , the inset shows a SEM image at larger magnification and the cracks can be clearly observed within the white circles, for instance.

An important role in the phase decomposition is expected to be played by the diffusion of the different species within the material during annealing at high temperatures. As it has been explained by different authors, the formation of alu-

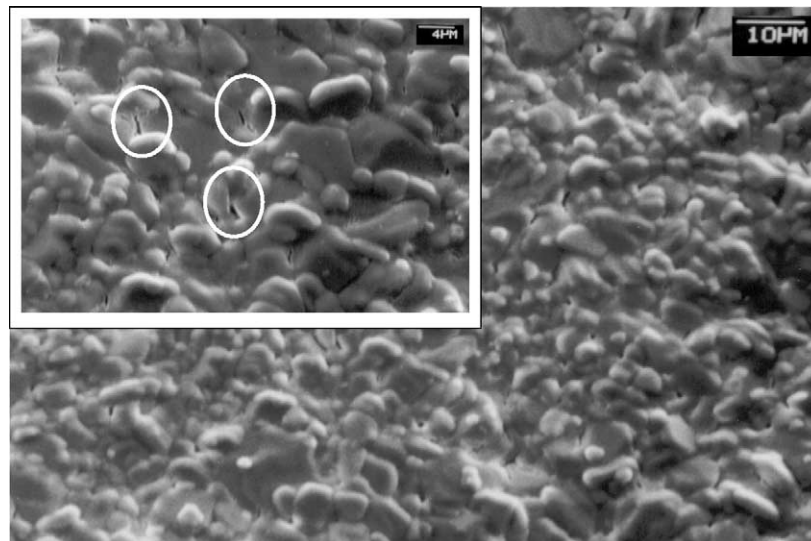


Fig. 7. SEM picture of $\text{Mg}_{0.6}\text{Al}_{0.8}\text{Ti}_{1.6}\text{O}_5$ film after annealing at 1100°C for 1 h. The presence of microcracks is evidenced by white circles in the inset.

Table 2
Surface chemical composition of $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$ films after firing at different temperatures, as measured by XPS

Firing temperature (°C)	Ti/Al (2.0)	Al/Mg (1.33)	Ti/Mg (2.67)
500	1.97	1.40	2.70
700	2.54	1.0	2.54
1100	1.92	0.84	1.62
1200	1.51	1.02	1.54

The nominal values are reported in brackets.

minium titanate at such low temperatures, if compared to the eutectoid one, is due to crystallization in conditions of limited diffusion.¹³ However, at higher temperatures, diffusion is becoming effective, as shown by the XPS results, and phase changes are in fact observed. The film surface chemical compositions, measured by XPS as a function of firing temperature, are reported in Table 2. At 500 °C a good accordance between the nominal and experimental values is observed. Conversely, at higher temperatures a discrepancy was found, associated to diffusion phenomena of the different species. In particular, a magnesium-rich layer was formed on the film surface, probably due to higher mobility of Mg with respect to Ti and Al ions. As a consequence, variation in the surface composition was detected, which was likely becoming important in the phase transformation in the material.

4. Conclusions

Sol–gel processing of $Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$ films has allowed the preparation of aluminium titanate phase stabilized with magnesia at temperatures much lower than those necessary for solid state reactions. The films have shown a thermal stability up to 90 h at 1150 °C. At longer annealing times the formation of microcracks on the film surface reduces the thermal endurance of the coatings. XPS analysis has revealed a diffusion of Mg ions towards the film surface at larger temperatures of firing.

Acknowledgement

ASI (Agenzia Spaziale Italiana) is gratefully acknowledged for financial support (Contract I/R/160/01).

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