Effect of Additives on Formation of Self-Supported Zircon Film by Sol–Gel Method

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ゾル–ゲル法によるジルコン独立膜の形成に及ぼす添加剤の効果

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Self-supported zircon films were successfully formed by heat-treating a gel prepared from the precursor solution of $\text{Zr}(\text{OC}_4\text{H}_9)_4$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ by the sol–gel method. The effect of additives, such as $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and CuCl_2 , on the formation of zircon film was examined. It was found that the addition of $\text{Cu}(\text{NO}_3)_2$ in precursor solution was effective for obtaining a single-phase zircon at low heat-treatment temperature. From thermal analyses and X-ray diffractometry, the crystallization temperature of zircon was found to be about 950°C. A zircon film with the size of 8 mm × 8 mm × 6 μm was obtained which did not contain any crack.

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1. Introduction

Zircon (ZrSiO_4) is one of candidates for high temperature refractory materials, because of its high thermal shock resistance, originating from its low thermal expansion coefficient.¹⁾ The powders of zircon have been synthesized by solid state reaction between ZrO_2 and SiO_2 fine particles and by hydrolysis of Zr- and Si-alkoxides.^{2)–7)} Much attention has been paid to the effect of additives, such as alkali halides and transition metal oxides, on its various properties.^{8)–12)} However, the fabrication of self-supported zircon thin films has scarcely been reported, probably because of the difficulty to carry out the hydrolysis of two alkoxides of silicon and zirconium at the same rate. In order to obtain the monolithic and homogeneous zircon thin films, the control of the hydrolysis reactions of Zr- and Si-alkoxides, and the formation of the gel films involving Zr–O–Si bonds seems to be important. If the zircon films could be formed through the sol–gel method in which reaction of two alkoxides is carefully controlled, their application at high temperature, such as the improvement of oxidation resistance of carbon materials coated with zircon film would be widened up, as we reported before.¹³⁾

In the present work, zircon thin films were successfully formed from the gel film prepared by controlling the hydrolysis rates of the precursor solution of Zr- and Si-alkoxides. The preparation conditions of zircon thin films were studied, with paying a special attention to the effect of additives.

2. Experimental procedure

In Fig. 1, the process for preparing zircon thin films is shown as a flow chart. Zirconium tetra-butoxide ($\text{Zr}(\text{OC}_4\text{H}_9)_4$, hereafter ZrBu) and silicon tetra-ethoxide ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS) were selected as starting materials. Since ZrBu is extremely sensitive to moisture, it was dissolved into 2-propanol. Then, triethanolamine ($\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, TEA) was added as a stabilizing agent in a molar ratio (TEA/ZrBu) of 2. The concentration of ZrBu was adjusted to be 0.05 mol·dm^{−3}. The resultant solution was sealed into a flask and then stirred at room temperature for 24 h. TEOS was dissolved into ethanol containing either

Fig. 1. Preparation procedure of zircon film.

$\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ or CuCl_2 with the concentration (100 × catalyst/(catalyst + TEOS)) of 2 or 10 mol%. After the addition of distilled water of which molar ratio to TEOS was

5, the solution of TEOS with a concentration of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ was refluxed at the boiling point for 48 h. Two alcoholic solutions of ZrBu and TEOS thus prepared were mixed to be a molar ratio (ZrBu/TEOS) of 1, then were used as a precursor for zircon. All these preparation processes were performed in dry nitrogen atmosphere.

The precursor solutions were spread on the teflon® sheets that were cleaned beforehand with acetone in order to remove the surface contaminants. The sol films on the sheets were kept standing at room temperature in air for 48 h, to proceed the hydrolysis-condensation reaction, gel films being obtained on the sheets. After peeled off from the teflon sheets, the gel films were dried at 80°C . The size of the gel films obtained was $10 \text{ mm} \times 10 \text{ mm} \times 10 \mu\text{m}$. Those gel films were heated up to different temperatures at a heating rate of 50°C h^{-1} and kept at respective temperatures for 1 h.

The gel films prepared were subjected to thermo-gravimetric and differential thermal analyses (TG-DTA; Rigaku, TG-8110). The structural change of the films with the heat-treatment temperature was examined by X-ray diffraction (XRD; Rigaku, RAD-VC) and infrared spectroscopy (FT-IR; JEOL, JIR-3505) using a KBr briquette method. The films obtained were also observed by scanning electron microscope (SEM; JEOL, JXA840).

3. Results and discussion

In order to prepare the homogeneous solutions consisting of ZrBu and TEOS, or to form Zr-O-Si bonds in the gel films, it is essential to control the hydrolysis reaction of each alkoxide. ZrBu is easily hydrolyzed, even by moisture in the atmosphere and give viscous sol, which forces the zirconium hydrolyzate to be segregated in the solution. Therefore, it was necessary to suppress such a rapid hydrolysis of ZrBu by adding TEA. On the other hand, since TEOS is so stable, the acceleration of its hydrolysis by using catalysts is necessitated. So, before mixing with ZrBu, TEOS was partially hydrolyzed by adding a catalyst and water.

The molecular level structure of the gels prepared from the precursor solutions containing ZrBu and TEOS was studied by FT-IR, in order to examine the formation of Zr-O-Si bonds in the gels. Figure 2 shows FT-IR spectra of gels prepared from the precursor solution with the additive concentration ($100 \times \text{catalyst}/(\text{catalyst} + \text{TEOS})$) of 10 mol%. For the gels added with $\text{Ni}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$, the absorption peaks observed around 1000 and 640 cm^{-1} are assigned to Si-O and Zr-O bonds, respectively. The peak around 900 cm^{-1} is that tentatively assigned to Zr-O-Si bonds by Mori et al.⁴⁾ In the case of the gel added with CuCl_2 , however, the absorption peak corresponding to Zr-O-Si bonds is broadened and its intensity is smaller than those in the gels added with $\text{Ni}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$. From these results, it was considered that the addition of nitrates, $\text{Ni}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$, was effective for controlling the hydrolysis of TEOS, and allowed the formation of Zr-O-Si bonds in the gel. The use of nitrates as catalyst may be more suitable than chloride, CuCl_2 , to control the hydrolysis of TEOS.

In Fig. 3, XRD patterns of the sample prepared from the alkoxide solution added with 10% $\text{Cu}(\text{NO}_3)_2$ and heat-treated at different temperatures are shown. No diffraction peaks are detected below 800°C , suggesting the amorphous state. Above 1000°C , the single phase of zircon is obtained. In Table 1, the formation of zircon detected by XRD is summarized for all samples, together with the results described above. Below 800°C , no diffraction peaks were detected in all samples. Above 1000°C , the samples containing 2% $\text{Cu}(\text{NO}_3)_2$ or 10% CuCl_2 formed zircon through the deposition of tetragonal ZrO_2 . However, only tetragonal ZrO_2 was

Fig. 2. FT-IR spectra of the gels prepared from the precursor solution at a concentration ($100 \times \text{catalyst}/(\text{catalyst} + \text{TEOS})$) of 10 mol%: (a) $\text{Ni}(\text{NO}_3)_2$, (b) $\text{Cu}(\text{NO}_3)_2$ and CuCl_2 .

Fig. 3. XRD patterns of the sample heat-treated at different temperatures for 1 h. The sample was prepared from the precursor solution added with 10 mol% $\text{Cu}(\text{NO}_3)_2$.

Table 1. Crystal Phase of the Samples Obtained by Heat-Treating the As-Prepared Gels at Different Temperatures for 1 h

Temperature / °C	Concentration (100 x catalyst / (catalyst+TEOS)) / %					
	Ni(NO ₃) ₂		Cu(NO ₃) ₂		CuCl ₂	
	2	10	2	10	2	10
800	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
900	t-ZrO ₂	t-ZrO ₂	N.D.	N.D.	t-ZrO ₂	t-ZrO ₂
1000	t-ZrO ₂	t-ZrO ₂	t-ZrO ₂	ZrSiO ₄	t-ZrO ₂	t-ZrO ₂
1100	t-ZrO ₂	t-ZrO ₂	t-ZrO ₂	ZrSiO ₄	t-ZrO ₂	ZrSiO ₄
1200	t-ZrO ₂	t-ZrO ₂	ZrSiO ₄	ZrSiO ₄	t-ZrO ₂	ZrSiO ₄

Note: N.D. means no detection of diffraction peaks

Fig. 4. TG-DTA curve of the gel prepared from the precursor solution added with 10% Cu(NO₃)₂.

detected in the samples added with Ni(NO₃)₂ or 2% CuCl₂, that is, no formation of zircon was observed up to 1200°C. From XRD results, it is found that the addition of Cu(NO₃)₂ or CuCl₂ in the precursor solution is suitable to obtain a single phase of zircon. The best catalyst among three used in the present work and its concentration in precursor solution for obtaining zircon is Cu(NO₃)₂ and 10%, because of the deposition of zircon from amorphous state almost without forming tetragonal ZrO₂.

Eventually, based on the results of FT-IR and XRD, it is very probable that nitrate ions catalyze the hydrolysis of alkoxides in the precursor solution more effectively than chloride ions and Cu²⁺ ions act as nuclei for zircon formation more effectively than Ni²⁺ ions.

Figure 4 shows TG-DTA analysis for the gel added with 10 mol% Cu(NO₃)₂. Two exothermic peaks with weight losses observed at 380 and 460°C are considered to be due to the combustion of organic compounds that are produced by the hydrolysis of alkoxides. The small exothermic peak without weight loss observed at 950°C is attributable to the formation of zircon, on the basis of XRD results.

SEM-micrographs of zircon film obtained by heat-treating at 1000°C are shown in Fig. 5. The surface of film looks smooth, and also no cracks and pores are observed (see Fig. 5(a)). The thickness of film obtained was about 6 μm (Fig. 5(b)), which was smaller than that of gel film, which should be due to the contraction caused by the crystallization of zircon.

(a)

← Film →

(b)

Fig. 5. SEM-micrographs of the surface (a) and the cross section (b) of zircon film obtained by heat-treating at 1000°C.

In conclusion, it was found that Cu(NO₃)₂ is more suitable as an additive for controlling the hydrolysis of starting alkoxides and the nucleation of zircon than Ni(NO₃)₂ and CuCl₂, in order to obtain crack-free self-supported films of single-phase zircon by the sol-gel method at relatively low temperatures as ~1000°C.

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