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Effect of sintering on TiO_2-impregnated alumina foams

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The effect of sintering on the bulk properties, morphology and phase composition of ultralight Al_2O_3 foams impregnated with TiO_2 was investigated in comparison with pure alumina foam in the temperature range of 900–1600°C in air. Impregnation was carried out by immersion of pre-sintered alumina foam in a sol of titanium isopropoxide-acetylacetone complex. The changes of the foam linear shrinkage, effective density and porosity were studied along with morphological evolution and relationship between these properties was demonstrated. Titania impregnation increased the linear shrinkage (LS) during sintering by a maximum of 5% relative to pure alumina foams. The change of LS and weight loss of TiO_2/Al_2O_3 foams lead to a final density of 0.19 g/cm^3 and porosity of 95%. The initial coating was found to develop a mosaic structure due to early shrinkage of the coating. After sintering at 1600°C the coating reacted with the underlying Al_2O_3 surface and became uniformly distributed. Finally, it was shown that the reacting TiO_2 layer formed the tialite (Al_2TiO_5) phase below 1400°C. This Tialite coating remained intact under 1200°C without stabilizers. *© 2002 Kluwer Academic Publishers*

1. Introduction

Porous ceramics, in general and cellular ceramics in particular have a wide spectrum of applications ranging from catalyst supports to thermal insulators [1]. The preparation and characterization of ultralight alumina foams with an extremely high porosity of 92–98% was recently reported [2, 3]. In addition to the pure component foams, it is important to develop multicomponent systems. For example, TiO_2 is often coated on surfaces due to its high reflectivity, as well as photocatalytic activity. TiO_2 exists in three crystalline modifications; anatase, brookite and rutile. The anatase phase is used in photocatalitic applications because of its photochemical activity [4]. The rutile phase, which is stable above 700°C is often used as a white pigment due to its refractive index. In this work pure alumina foams were coated by impregnation with a sol of titanium isopropoxide-acathylacetate complex followed by drying and sintering at 1600°C.

The morphological and compositional changes occurring during sintering of the ultralight ceramic foams [3] studied here, are essentials to the final foam properties [5, 6]. Solid state sintering involves two main phenomena occurring simultaneously: One is pore shrinkage, densification, and thus general dimensional shrinkage and the second is grain growth [7]. The main objective of presented work is to coat the ultralight alumina foams with Titania and to investigate the effect of sintering conditions on the macro and microstructures of alumina/titania foams, their physical properties and phase development.

2. Experimental

2.1. Specimen preparation

Ultralight alumina foams with porosity of 95–98% were prepared using the method described elsewhere [2, 3]. Titania was introduced by impregnation into the alumina foams, which were pre-sintered at 1600°C for 1 hr. After the initial sintering, the bulk alumina foams were cut into rectangular shapes with dimensions of approximately 15 × 10 × 5 mm. Impregnation was carried out by immersion of these samples in a sol of titanium isopropoxide, prepared from Titanium isopropoxide, acetylacetone, isopropanol and water [8]. After the immersion and drying at room temperature for 2 hrs, the impregnated foams as well as pure alumina blank samples were reheated, (300°C/hr) in air at 900°C, 1100°C, 1400°C and 1600°C for 1 hour. The average titania loading in the sintered foam was 10wt%.

2.2. Sample characterization

The weight and linear dimensions of each sample were measured before and after sintering and normalized relative to their values after the initial sintering at 1600°C. The density and porosity were then calculated based on the measured weight and dimensions. Image analysis of foams sintered at different temperatures was performed using an SEM (JEOL JSC 5400, Japan). The titania distribution in the alumina matrix was determined by X-ray mapping of Ti and Al by EDS (Noran Instruments, Middleton, WI, USA).

Phase transformations during heat treatment were studied by XRD analysis using a D5000 powder diffractometer (Siemens, Germany) employing Cu-K$_\alpha$ radiation.

Thermal analysis (TGA/DTA) was conducted in a Setaram TG-92 unit under flowing air (30 ml/min) with a heating rate of 5°C/min and sample mass of 40–50 mg.

3. Results and discussion

3.1. Linear shrinkage

Pure alumina foams show a significant isotropic linear shrinkage (LS) of approximately 15% after the initial sintering at 1600°C. The LS during subsequent heat treatments (in the 900–1600°C range) is presented in Fig. 1. For unimpregnated foam (blank) the shrinkage was found to be lower than 1.5% (Fig. 1) in the entire temperature range. A significant increase of LS in comparison with blank was observed for impregnated foam, its value at 1600°C was about 6%. The difference in LS between blank and impregnated foam rose with temperature and reached 4.5–5% at 1600°C. This data points to a significant effect of impregnated titania on the shrinkage of alumina foam. The mechanism leading to this enhanced shrinkage will be discussed in subsequent sections.

3.2. Thermal analysis

During sintering at all temperatures in the 900–1600°C range, the weight loss (WL) of dried impregnated samples was about 10–15%. It was caused by desorption of solvent and decomposition of the organic part of the Ti complex as shown in Fig. 2a and b.

The four main stages during heating are outlined below:

(a) RT- ~150°C—endothermic desorption of adsorbed solvent with WL of about 5% wt of initial weight and highest WL rate;

(b) 150–420°C—intense exothermic oxidation of organics accompanied by some large overlapped peaks with WL of ~13% and high WL rate;

(c) 420–750°C—exothermic oxidation of organic residuals with a wide exothermic peak and WL of about 1% and very low WL rate;

(d) $T > 750$°C—no detectable WL or DTA signal were observed. It may be concluded that only stable inorganic components remain above 750°C.

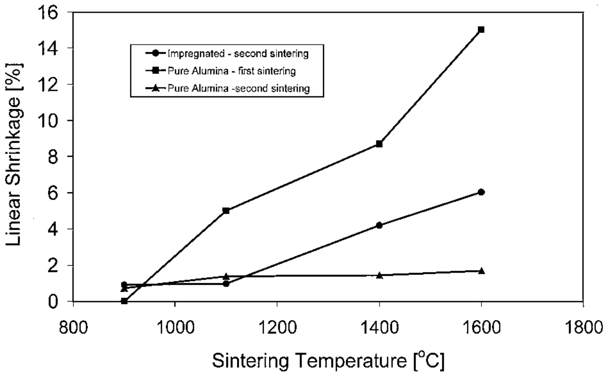
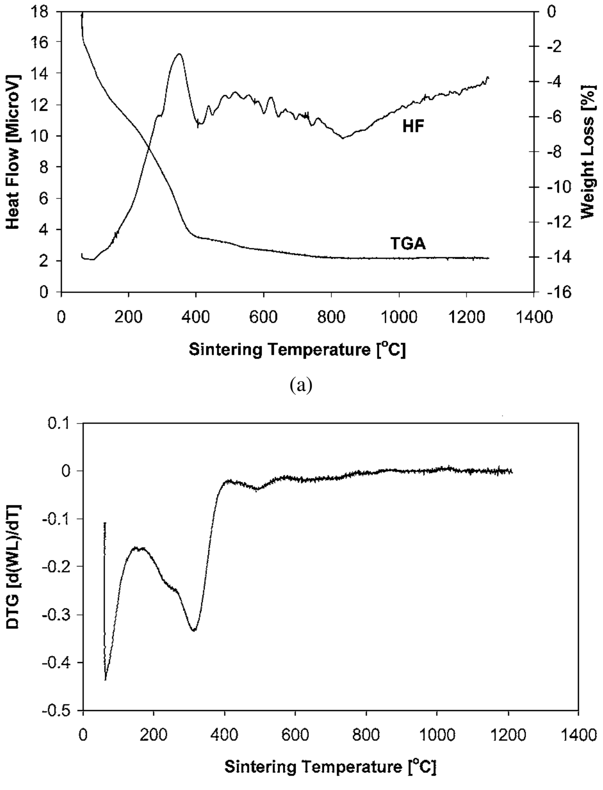


Figure 1 Linear shrinkage vs. sintering temperature (1 hr at the noted temperature), of three types of foams: ▲ - Pure alumina foam during second sintering, ■ - Pure alumina foam during first sintering, ● - Titania Impregnated foam during second sintering.



(a)

(b)

Figure 2 Thermal analysis of a titania/alumina foam after impregnated and drying at room temperature, (a) weight loss and heat flow curves, (b) DTG curves.

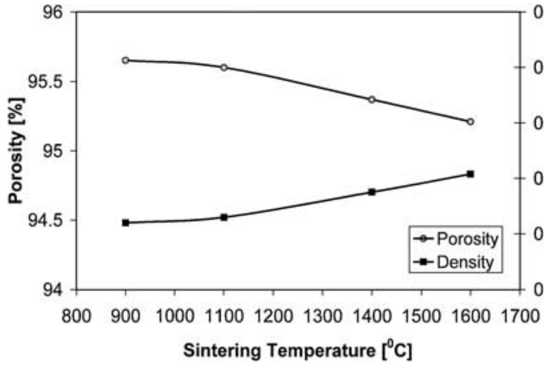


Figure 3 Porosity and density vs. sintering temperature of impregnated foam samples.

3.3. Density and porosity

Slight changes in the foam's effective density and porosity were obtained during sintering due to low linear shrinkage and weight loss. Fig. 3 presents both density and porosity changes vs. Temperature during sintering. In the 900°C–1600°C range the density increased from an initial value of 0.17 gr/cm^3 to 0.19 gr/cm^3, a change of only ~10%. This final density is still within the range typical of ultralight ceramic foams.

Porosity (void fraction was calculated from the effective density and the density of solid alumina and/or titania, according to: $P = 100^*(1 - \rho/\rho_{\text{Solid}})$, where P is porosity, ρ is foam effective density (gr/cm^3), and ρ_{Solid} is alumina density (4 gr/cm^3), and titania density (3.9 gr/cm^3).

As can be seen from Fig. 3, the largest decrease in porosity during the sintering at 1600°C was less than 1%, with values of around 95%. It is obvious that the

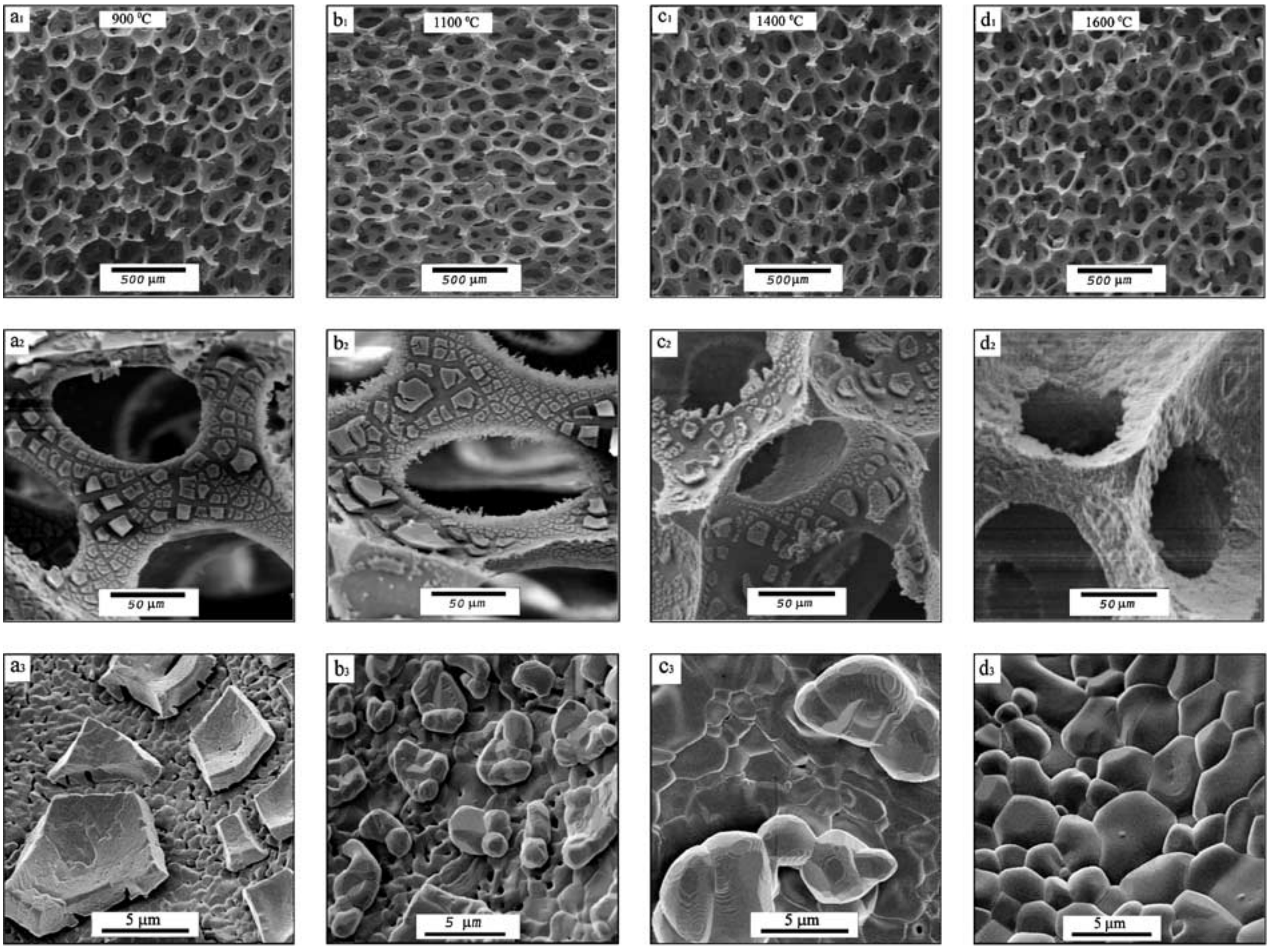


Figure 4 SEM images of titania impregnated samples at different sintering temperature and magnifications.

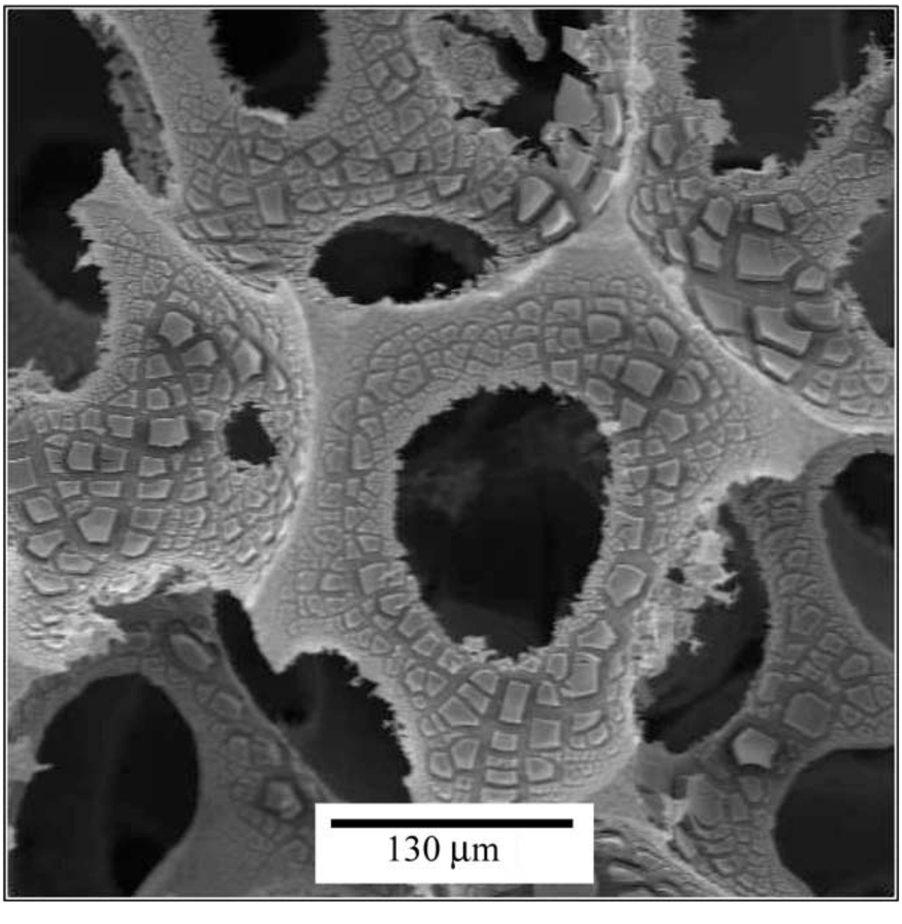


Figure 5 SEM image of titania impregnated foam, heated to 450°C.

increase in density caused the decrease in the porosity; since the density change was not so notable, the porosity change is almost negligible. Based on the above, we can conclude that impregnated titania only weakly influences the final void fraction in the initially sintered foam.

3.4. Morphology development and titania distribution

In this paper the structure evolution of the titania coating as a function of temperature is investigated. At low magnifications (×50), the cellular macrostructure (bubbles) is visible but the coating cannot be distinguished. However, at higher magnifications (X500–X2000), the coating is visible. The important coating characteristics include its uniformity, thickness, shape and the position of individual grains within the coating.

Three images were obtained from each sample: one at small magnification (×50) in order to capture the overall cellular macrostructure, one at medium magnification (×500) to permit observation of the overall coating pattern and finally, one at larger magnification (×2,000) to study the microstructure of the coating elements.

Fig. 4 consists of a matrix with 12 SEM images: categories a–d represents the different temperatures (a - 900°C, b - 1100°C, c - 1400°C, d - 1600°C). The index (1–3) represents the magnification (1 - ×50, 2 - ×500, 3 - ×5000).

The rows allow comparison of samples with the same magnification but different sintering temperatures. Fig. $4a_1$–d_1 (magnification ×50) are virtually identical. All samples are open-cell foams with no visible difference in macrostructure inspite of the different sintering temperature. Fig. $4a_2$–d_2 (magnification ×500) reveal the coating pattern. At 900–1400°C the coating is not continuous and consists of broken islands, most of which are polygons with well-defined edges. The planar arrangement resembles a mosaic, which would form a continuous surface if the islands could be pulled together. This pattern clearly indicates that the coating was originally continuous, and due to internal shrinkage at some lower temperature it broke into the islands shown in Fig. $4a_2$ and a_3. Another indication of the shrinkage of the TiO_2 layer is seen by the concave nature of the islands on the Al_2O_3 under layer. As the sintering temperature rises, the islands become more granular as seen in Fig. $4b_3$. Fig. $4c_3$ shows that morphological changes are also occurring in the surface below the TiO_2 islands. The initial porosity in the Al_2O_3 substrate seen in Fig. $4b_3$ is gone and the surface grains are clearly larger. After sintering at 1600°C a complete assimilation of the islands into the alumina matrix occurs, forming a new layer with well defined microstructure shown in Fig. $4d_3$. The surface seen in $4d_2$ does not look smooth at this stage, but the islands that originally covered it are clearly gone.

The pattern of mosaic-like islands can be explained using DTA/TGA, optical and SEM data. After drying the fresh film at RT the titania complex forms a continuous yellow film over the alumina matrix with only a few cracks. Further heating at relatively low temperatures leads into cracking the film into islands and shrinkage of individual islands. In the range of 150–420°C the initially yellow titania complex film decomposes and the color first changes from yellow to brown and then to black-gray at 450°C. The 8% weight loss occurring at 150–420°C, discussed previously, reflects the complex decomposition and formation of the TiO_2 phase. The SEM picture of the film formed at 450°C in air, shown in Fig. 5, confirms the island formation at low temperatures.

To determine the location and distribution of titania in the foam, an X-ray mapping of impregnated foams sintered at different temperatures was systematically conducted. The functions of this mapping work were: (a) examination of the overall titania distribution at low magnification on the foam's macrostructure and (b) clear chemical identification of the islands and background composition. Each SEM/EDS observation

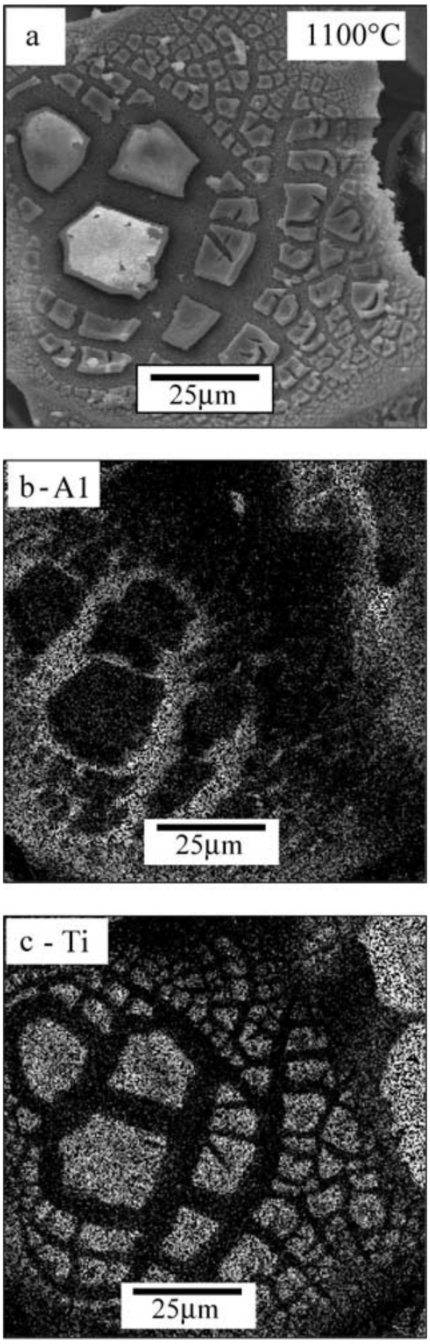


Figure 6 SEM/EDS images of titania impregnated at 1100°C; (a) SEM image; (b) Al scanning; (c) Ti scanning.

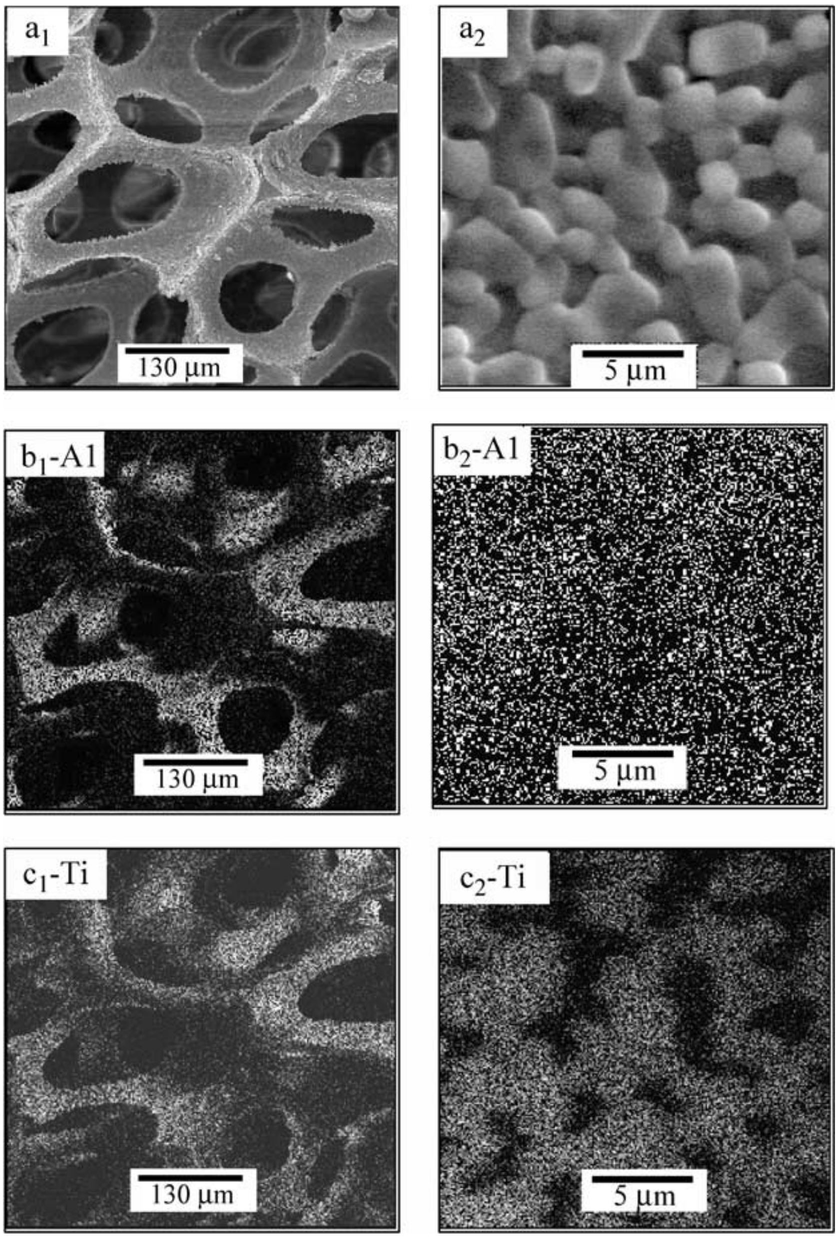


Figure 7 SEM/EDS images of titania impregnated (1) macrostructure and (2) microstructure at 1600°C; (a) SEM image; (b) Al scanning; (c) Ti scanning.

consists of three interrelated images of the same region: (a) SEM image, (b) Aluminum X-ray map, and (c) Titanium X-ray map. Fig. 6a shows the island layout in a sample sintered at 1100°C at an ×1000 magnification. The EDS maps of Al and Ti (6b–c) show the distribution of Ti and Al at this level. The two maps represent clearly that the broken islands are TiO_2 while the background matrix is alumina.

Samples heated to 1600°C were analyzed at two different magnifications in order to follow the interaction of the titania islands with the alumina surface. Fig. 7 consists of 6 images from the same sample where the low and high magnifications are indicated by index 1 and 2, respectively. It can be seen that after sintering at 1600°C, the titania distribution in the alumina matrix is homogeneous at all the magnifications. At 1600°C the originally distinct TiO_2 islands have disappeared and no cracks were observed in this layer even at high magnification. Identification of the phases in this new layer is described in the next section.

3.5. Phase formation

The SEM and EDS results, discussed in the previous section indicated that between 1400°C and 1600°C a new phase was formed in the coating layer. The phase composition of sintered foams affects their final properties and chemical stability [9]. Therefore, the phase development in the titania coated alumina foam was thoroughly investigated to verify the possibility of bicomponent phases formation. According to phase diagrams [10] alumina and titania form the binary phase (Al_2TiO_5) tialite, which appears in two phase modifications: α and β. α-Al_2TiO_5 is high temperature modification with congruent melting point at 1860°C and equilibrium phase transition to β-Al_2TiO_5 at 1820°C. The β-Al_2TiO_5 is stable under equilibrium conditions [10] in the interval of 1200–1820°C. Usually, below 1200°C β-Tialite is unstable due to eutectoid decomposition followed by phase separation into α-Al_2O_3 and rutile TiO_2. This instability is the main reason for difficulties in production of tialite-based ceramics by conventional

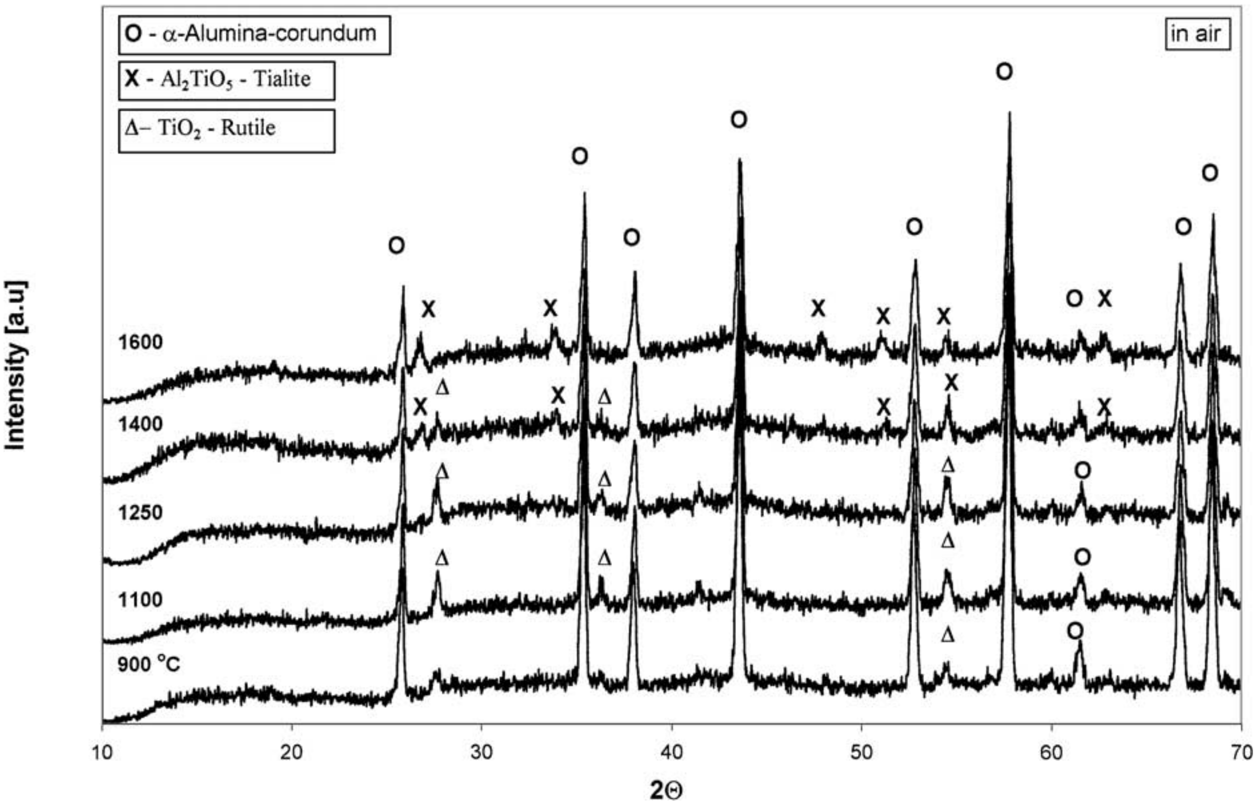


Figure 8 X-Ray patterns of five samples at different sintering temperature.

methods. Recently, some publications were dedicated to hydrolytic [11, 12] and nonhydrolytic sol-gel synthesis of β-Al_2TiO_5[13], where the possibility of tialite preparation at relative low temperatures was demonstrated. But the problem of tialite phase separation still exists and is under investigation [13].

In the present work, the phase formation in the titania impregnated alumina foams was studied in the 900–1600°C range as shown by the XRD patterns in Fig. 8. At 900°C, two phases were recognized: rhombohedral α-alumina (Corrundum) and tetragonal titania (Rutile). It should be pointed out again, that the foam matrix was presintered at 1600°C, which is why α-alumina is present already at 900°C. The titania peaks at 900°C were very weak but reproducible and defined enough to be identified. At 1100°C and 1250°C the titania peaks become more intense, but the phase composition remained the same: a mixture of Corundum and Rutile. A product of alumina and titania solid phase interaction was clearly identified at 1400°C: numerous sharp peaks of β-Al_2TiO_5 phase has been detected along with a reduction of rutile peaks. At 1400°C the system included three phases: corrundum, rutile and β-Al_2TiO_5. At 1600°C, the titania phase disappears converting completely into tialite. The formation of tialite continuos layer at relatively low temperature on the surface of the sol-gel processed alumina foam is well correlated with tialite derived via sol-gel processes [11–13].

It should be pointed out, that the tialite layer remained stable below 1200°C, (during cooling) without additions of any stabilizers [11]. The sintered samples were stored in ambient conditions and change of morphology and phase composition was not observed at least for a few months.

Despite the fact that the alumina matrix was previously sintered at high temperature, tialite formation at 1200–1400°C affects the foam properties such as: (a) The strong increase of the linear shrinkage above 1200°C (Fig. 1). (b) Significant change of the porosity and density curves slope occur above $\sim$1100°C (Fig. 3). The effect of tialite formation was also essential in microstructure development of the foam's coating: from mosaic like pattern of islands, to a homogeneous, continuous coating. Disappearance of the islands and their assimilation with the Alumina matrix can be clearly seen at the SEM/EDS images of the 1600°C (Figs 4d_3 and 7).

In previous work [14], the effect of tialite formation on the foam properties was more dramatic leading to a linear shrinkage of $>30\%$ at 1600°C whereas in the current work the linear shrinkage under the same conditions was only 6%. The main reasons for this drastic difference are: 1. in the previous work the titania was incorporated *in situ* during the foaming procedure and thus was homogeneously distributed in the foam volume, and 2. The alumina matrix was not previously sintered and tialite formation was realized during primary sintering.

4. Conclusions

The formation of TiO_2 coating on the surface of ultra-light alumina foams and the effect of sintering on the foam's linear shrinkage, morphology and phase composition were investigated up to 1600°C in air. The titania was incorporated by impregnation of the presintered alumina foam with a sol of titanium isopropoxide-acetylacetone complex followed by drying and heat treatment at various temperatures.

Based on DTA/TGA investigations, four distinct stages were defined which include an endothermic solvent evaporation at RT-150°C, an exothermic sharp oxidation in the 150–420°C, a wide oxidation of residual organics at 420–750°C, and constant weight heating above 750°C. The overall weight loss (WL) in the heating process is 10–15 wt%.

Titania impregnation increased the linear shrinkage (LS) during sintering compared to pure alumina foams. The difference in LS rose with temperature and reached 4.5–5% with an overall LS of 6% at 1600°C. The change of LS and WL of TiO_2/Al_2O_3 foams lead to densification of 10% at final density of 0.19 g/cm^3 and porosity of 95%.

Morphology development and titania distribution were investigated extensively for samples obtained at different stages of heat treatment. The following evolution of the coating layer structure was observed as function of temperature: (a) continuous yellow film of titanium-organics complex with a few cracks existed after drying at RT, (b) heating of these samples in the range of 150–420°C caused the oxidative decomposition of Ti-complex film and formation of mosaic-like pattern of islands, (c) further of heating to 750°C lead to final decomposition of heavy organics along with titania formation, (d) finally, at 1600°C the mosaic elements merge into the alumina matrix and form a layer with tialite (β-Al_2TiO_5) structure.

The unconventional formation of tialite at relatively low temperatures and its stability under 1200°C without stabilizers should be pointed out. The long-term stability of this layer at temperatures below 1200°C is interesting and should be further investigated.

Acknowledgments

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