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Effect of Excess SiO_2 on the Reaction Sintering of Aluminium Titanate–25 vol% Mullite Composites

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Abstract: A stepwise alkoxide hydrolysis processing was used to prepare aluminium titanate–25 vol% mullite composite powders. The effect of three levels of excess SiO_2 (1, 3 and 5 wt%, expressed relative to Al_2TiO_5) on densification, microstructure, mechanical strength and thermal expansion has been investigated. The addition of excess SiO_2 reduced the constrained effect caused by the formation of Al_2TiO_5 and mullite. After the formation of Al_2TiO_5 and mullite, the densification rate was enhanced for the samples containing excess SiO_2. These effects can be attributed to the presence of a liquid phase at the firing temperatures. The presence of liquid phases during sintering promoted grain growth of Al_2TiO_5 and also the formation of acicular mullite. The mechanical strength of the composition with 3 wt% excess SiO_2 showed a three-fold improvement over the sample without excess SiO_2, whereas the corresponding thermal expansion was still relatively low ($\sim 1.3 \times 10^{-6}\ K^{-1}$ from 20 to 1000°C). The reduced porosity was believed to be the predominant factor contributing to the improvement of the mechanical strength © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Catastrophic failure of engineering ceramic materials generally happens when they are used in severe thermal environments due to large thermal stresses developed during abrupt temperature changes. Thermal stresses are a function of thermal expansion, thermal conductivity, strength and Young's modulus. Since a near-zero expansion of a material can minimize thermal stresses during temperature changes, much work has been done to search for very low thermal expansion materials for severe thermal shock applications.[1–4] Aluminium titanate (Al_2TiO_5) has been recognised as a low expansion material for several decades.[5–7] It has been evaluated for insulating components in automotive engines, such as manifolds, portliners and heads of piston,[8,9] where thermal insulation and thermal shock resistance are required. It has also found applications in the metallurgical industries.[10] However, a wider use of this material is limited by two well recognised problems: first, the very weak mechanical strength due to the thermal expansion anisotropy-induced microcracking, and second the decomposition of Al_2TiO_5 into α-Al_2O_3 and TiO_2 (rutile) between about 800 and 1280°C.[11]

In recently developed Al_2TiO_5–mullite composites,[12–16] the mechanical strength was improved while the favourable low thermal expansion of Al_2TiO_5 could be maintained at medium values between that of Al_2TiO_5 and mullite. Furthermore, the decomposition propensity of Al_2TiO_5, which is the other drawback of Al_2TiO_5, could be decreased in this composite system.[12,16]

Since the engineering properties of Al_2TiO_5-based materials strongly depend on the microstructure control, various powder processing routes, namely conventional mixing oxides methods,[17] gel-coating,[18] or chemical precipitation,[15,16] have been attempted to obtain the required microstructure. However, difficulties, such as a poor sinterability, are generally encountered, especially

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*To whom correspondence should be addressed in reaction sintering composite systems. This was believed to be due to the rapid grain growth of Al_2TiO_5 during its formation process[19,20] and also to the constrained effect of second phases,[21,22] thus yielding a porous material.

It is known that SiO_2 can enhance densification of Al_2TiO_5[23,24] by the formation of a liquid phase during sintering. However, an exaggerated grain growth and microcracking can occur, decreasing the mechanical strength. The purpose of this work is to investigate the effect of excess SiO_2 on the densification, microstructure and properties of a Al_2TiO_5–25 vol% mullite composite prepared from a stepwise alkoxide hydrolysis processing.

2 EXPERIMENTAL PROCEDURE

Aluminium sec-butoxide ($Al(OC_4H_9)_3$, Merck reagents), titanium butoxide ($Ti(OC_4H_9)_4$ Merck reagents) and tetraethylorthosilicate ($Si(OC_2H_5)_4$ TEOS, Af reagents) were used as sources of Al_2O_3, TiO_2 and SiO_2, respectively. The synthesis of Al_2TiO_5-25 vol% mullite composite powders with 0, 1, 3 and 5 wt% of excess SiO_2 relative to the weight of Al_2TiO_5, (hereafter noted as S0, S1, S3 and S5, respectively) were carried out by the following procedure: after weighing, TEOS was dissolved into a definite volume of distilled water to obtain a 0.1 M TEOS solution. This transparent solution was then heated and vigorously stirred at 70°C under reflux conditions for 8 h. The other solution was prepared by dissolving the required amount of $Al(OC_4H_9)_3$ and $Ti(OC_4H_9)_4$ into absolute ethanol. The hydrolysis of $Al(OC_4H_9)_3$ and $Ti(OC_4H_9)_4$ was carried out by mixing the hydrolysed TEOS solution and the $Al(OC_4H_9)_3$ and $Ti(OC_4H_9)_4$ ethanolic solution together at room temperature. A strong mechanical stirring was used during the whole processing. After stirring 2 h, the mixture was freeze dried. After being calcined at 500°C for 1 h to remove the organic residues, the resulting powders were milled in a planetary ball mill for 8 h, using absolute ethanol as the milling medium, and then dried in an oven at 80°C.

The as-obtained powders were pressed into bars (3.5×5×50 mm) by first uniaxial pressing at 50 MPa and then isostatic pressing under 200 MPa. Sintering was performed in a box furnace, at a heating rate of 5°C min^{-1} up to 1600°C, holding 4 h and then cooling down at a rate of 5°C min^{-1}. The X-ray diffraction analysis (XRD) was carried out in a diffractometer (D/max-C, Rigaku) using CuK_α radiation, voltage 40 kV, electric current 20 mA. The powders for the XRD experiments were obtained by grinding the sintered samples. The morphology of the sintered specimens was observed by scanning electron microscopy (SEM, Hitachi, S-4100) in the backscatter mode. The shrinkage behaviour of the powder compact was recorded by a dilatometer (LINSEIS series), at a heating rate of 5°C min^{-1} up to 1600°C, with a soaking time of 4 h. The corresponding densification curve was calculated assuming isotropic shrinkage and using the green density as the initial reference. The green and fired density was measured by the Archimedes method using mercury. The thermal expansion behaviour of the sintered body was also measured by dilatometry at a heating rate of 5°C min^{-1} up to 1400°C and then at a cooling rate of 5°C min^{-1} down to 350°C. A SHIMADZU testing machine (Autograpa, AG-A series) was used to measure the three-point flexural strength. The specimens were polished with silicon carbide abrasive paper (No.1000) before measurements. The typical sample dimension is 2.5×3.5×40 mm. The span length was 20 mm and the crosshead speed 0.5 mm min^{-1}. Each data point is the average of 4–5 bars.

3 RESULTS AND DISCUSSION

3.1 Densification and microstructure

The relative density of the sintered samples is presented in Fig. 1, where the theoretical density values were calculated from the initial composi-

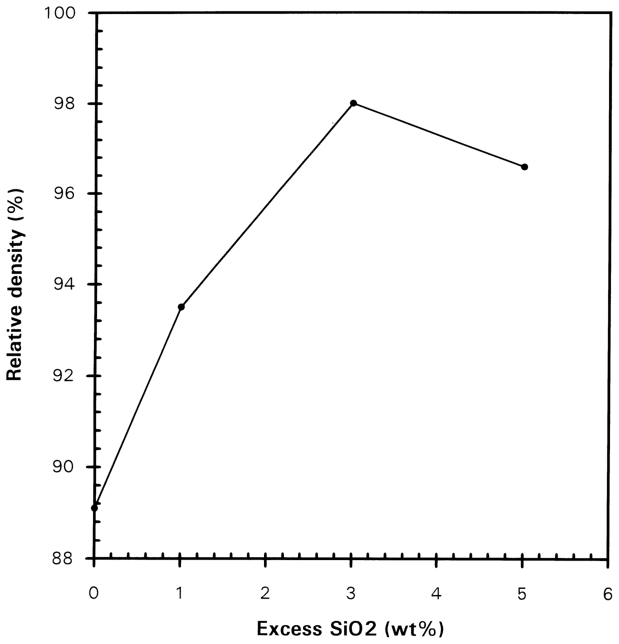

Fig. 1. Relative density of aluminium titanate–mullite composites vs excess SiO_2 content for samples sintered at 1600°C with a soaking time of 4 h.

tions (assuming that the reactions are complete and that excess SiO_2 forms glass phases with a density of 2.4 g cm^{-3}). The addition of excess SiO_2 has a pronounced effect on the final density of the composite. The density increases with the increase of the amount of SiO_2 up to 3 wt% where around 98% of the theoretical density was achieved. For 5 wt% excess SiO_2, the density is lower.

The sintering processes were also monitored by dilatometry. Figure 2 gives the densification curves for the S0, S1, S3 and S5 samples. Some differences in the densification behaviour of the various samples are observed. The S0 sample, without excess SiO_2, shows a high contraction rate before ~1400°C, followed by a broad, pronounced plateau which is associated with the formation of Al_2TiO_5 and mullite. During the dwelling time, the densification rate slows down. The samples with excess SiO_2 show two separate plateaux. These plateaux are smaller and smoother than that of the S0 sample. It seems that the presence of excess SiO_2 changes the Al_2TiO_5 and mullite formation kinetics. The subsequent densification of these samples are not affected by the process of Al_2TiO_5 and mullite formation and the density can quickly exceed that of the sample without excess SiO_2.

SEM photographs of the sintered samples are shown in Fig. 3. For the left side photos, obtained with a low magnification, it can be seen that non-homogeneous microstructures with dense and porous regions were obtained for the sample without excess SiO_2, clearly showing that the stepwise alkoxide hydrolysis processing used does not achieve enough uniformity in the chemical and/or physical characteristics of the composite precursors. A high degree of homogenization is progressively achieved when excess SiO_2 is added to the composite composition, inducing a more homogeneous presence of a liquid phase during the sintering process.

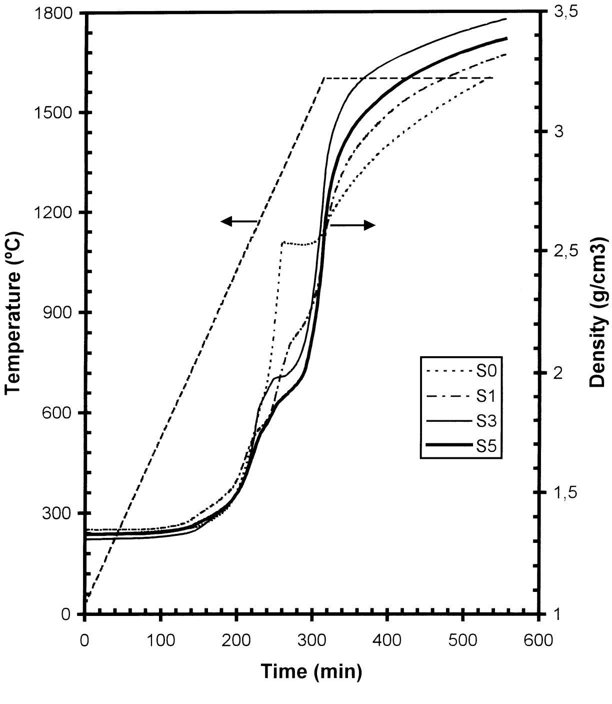

Fig. 2. Densification curves of powder compacts S0 (0 wt% excess SiO_2), S1 (1 wt% excess SiO_2), S3 (3 wt% excess SiO_2) and S5 (5 wt% excess SiO_2), at a heating rate of 5°C min^{-1} up to 1600°C, holding for 4 h.

The high magnification photos, obtained from dense areas in the respective samples, show clearly the effect of the SiO_2 additions on the microstructure of the sintered samples. A microstructure showing equiaxed grains of aluminium titanate and mullite is progressively substituted by a microstructure showing elongated tendency for the grains of both phases. The presence of a silica rich phase at the sintering temperature is known to produce acicular grains of mullite[25,26] and bigger grains of aluminium titanate[23] and also to enhance the densification of these monophasic materials. Both effects are retained in the aluminium titanate-mullite composite with the liquid phase helping to overcome the densification constraints caused by the presence of the second phase.

3.2 Mechanical strength and thermal expansion

The effect of excess SiO_2 on the room temperature three-point bending strength is shown in Fig. 4. The mechanical strength markedly increases with the addition of excess SiO_2. Slight variations due to the variation of the SiO_2 content shown in the figure are probably due to variations in the final density achieved by the various samples. Microstructure effects are difficult to interpret but it should not be forgotten that the result for the sample without excess SiO_2 is from a very poor non-uniform microstructure.

The thermal expansion behaviour of the sintered samples during the heating and cooling cycles is shown in Fig. 5. The samples show a pronounced hysteresis loop, characteristic of monophasic anisotropic or composite materials having different expansion coefficients in which large stresses are easily developed. The four consecutive stages, described previously for Al_2TiO_5 containing samples can be observed.[18] The low expansion corresponding to the closing of microcracks extends up to 1200°C. The samples containing excess SiO_2 present lower thermal expansion coefficients than that of the sample without excess SiO_2, the thermal expansion coefficient of the S3 sample being the lowest of all. The turning temperature points in the cooling curves represent the temperature of reopening of microcracks at ~600°C. The amount of expansion below this turning point has been correlated with the density of microcracks present in the cooled samples, which on the other hand controls the expansion behaviour on heating.[27] The percentage of expansion occurring for each sample between the turning point and 350°C is 0.094,

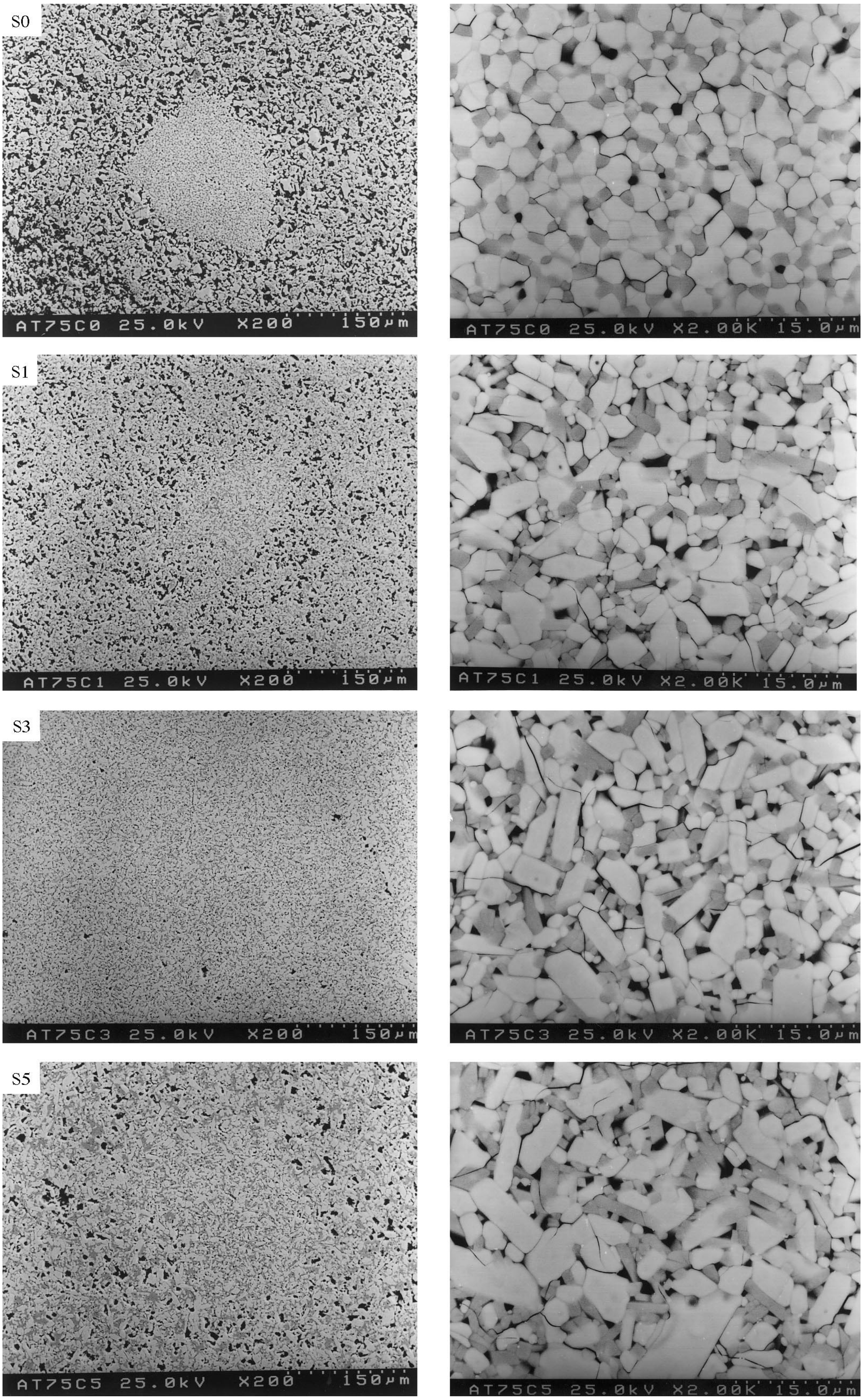

Fig. 3. SEM photographs of the samples S0 (0 wt% excess SiO_2), S1 (1 wt% excess SiO_2), S3 (3 wt% excess SiO_2,) and S5 (5 wt% excess SiO_2) sintered at 1600°C, during 4 h.

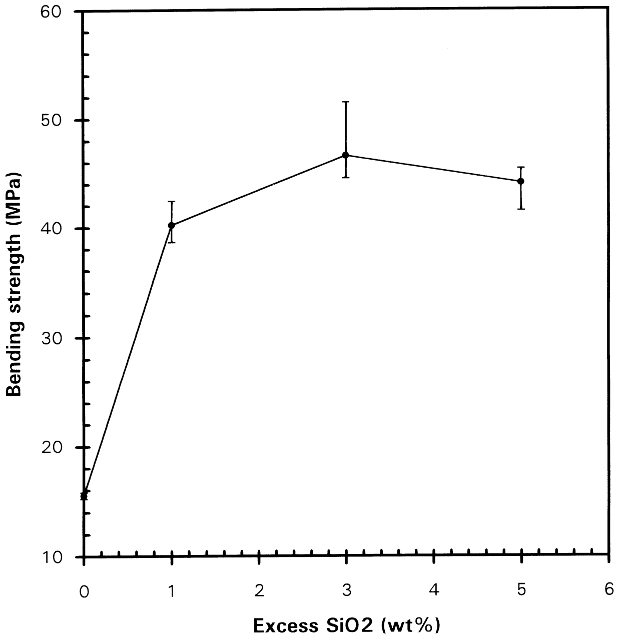

Fig. 4. Changes of bending strength of the sintered samples with the excess SiO_2 content.

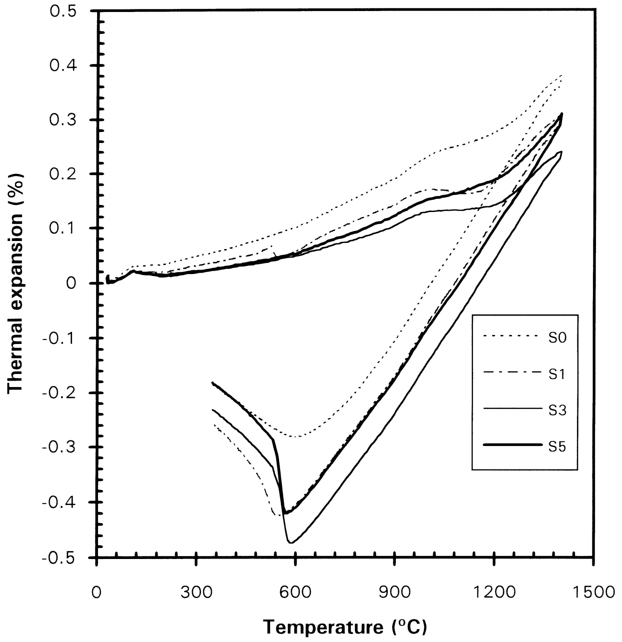

Fig. 5. Thermal expansion curves of the samples S0 (0 wt% excess SiO_2), S1 (1 wt% excess SiO_2), S3 (3 wt% excess SiO_2) and S5 (5 wt% excess SiO_2), at a heating and cooling rate of $5°C\,min^{-1}$.

0.165, 0.241 and 0.235%, respectively for the S0, S1, S3 and S5 samples. From these results, it can inferred that the S3 sample, which shows the lowest of the expansion coefficients, is the one with more extensive microcracking. The higher density and the more homogeneous microstructure of this sample, containing 3 wt% excess of SiO_2, is responsible for the higher bending strength value observed.

4 CONCLUSIONS

Aluminium titanate–25 vol% mullite composite powders with three levels of excess SiO_2 were prepared by stepwise hydrolysis of $Si(OC_2H_5)_4$, $Al(OC_4H_9)_3$ and $Ti(OC_4H_9)_4$.

The addition of excess SiO_2 can enhance densification of the composites by the formation of a liquid phase at the sintering temperatures. The presence of a liquid phase during sintering promoted the grain growth of Al_2TiO_5 and the formation of acicular mullite.

The mechanical strength was improved with the addition of excess SiO_2, chiefly due to the enhancement of the densification. The highest strength was achieved when 3 wt% excess SiO_2 was added, whereas the thermal expansion coefficient for the corresponding sample was maintained at a relatively low value ($\sim 1.3\times 10^{-6}\ K^{-1}$ from 20°C to 1000°C).

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REFERENCES

1. LIMAYE, S. Y., AGRAWAL, D. K., ROY, R. & MEHROTRA, Y., Synthesis, sintering and thermal expansion of $Ca_{1-x}Sr_xZr_4P_6O_{24}$—an ultra-low thermal expansion ceramic system. *J. Mater. Sci.*, **26** (1991) 93–98.
2. ROY, R., AGRAWAL, D. K., ALAMO, J. & ROY, R. A., A new structural family of near-zero expansion ceramics. *Mater. Res. Bull.*, **19** (1984) 471–477.
3. PARKER, F. J., Al_2TiO_5–$ZrTiO_4$–ZrO_2 composites: a new family of low-thermal expansion ceramics. *J. Am. Ceram. Soc.*, **73** (1990) 929–932.
4. ZHANG, B. & GUO, J. K., Thermal shock resistance of $KZr_2P_3O_{12}$–$SrZr_4P_4O_{24}$ ceramics. *J. Eur. Ceram. Soc.*, **15** (1995) 929–933.
5. LANG, S. M., FILLMORE, C. L. & MAXWELL, L. H., The system peryllia–alumina–titania: phase relations and general physical properties of three component porcelains. *Res. Natl. Bur. Stand.*, **48** (1952) 298–312.
6. MOROSIN, B. & LYNCH, R. W., Structure studies on Al_2TiO_5 at room temperature and at 600°C. *Acta Cryst.*, **B28** (1972) 1040–1046.
7. HENNICKE, H. W. & LINGENBERG, W., The formation and decomposition of aluminium titanate—II The decomposition reaction of aluminium titanate. *cfi/Ber.DKG*, **63** (1986) 100–106.
8. DWORAK, W. & FINGERLE, D., Ceramic materials for engines. *Br. Ceram. Trans. J.*, **86** (1987) 170–178.
9. BALTMANNSWEILEI, U. D., AICHWALD, H. O., HOCHDORF, D. F., LEONBERG, U. K., RÖNNINGE, M. J. A. H. & NYKVARN, B. N. J. P., Cylinder head of a piston engine. U.S. Patent 4524732, 25 June, 1985.
10. COOR, D., Application of aluminium titanate as thermocouple protection tubes in the molten aluminium

industry. In *Ceramic Transactions, Vol. 52, Low expansion materials*, ed. D. P. Stinton & S. Y. Limaye. American Ceramic Society, Westerville, OH, 1995, pp. 247-254.

11. KATO, E., DAIMON, K. & TAKAHASHI, J., Decomposition temperature of β-Al_2TiO_5. *J. Am. Ceram. Soc.*, **63** (1980) 355–56.
12. YANO, T., NAGAI, N., KIYOHARA, M., SAITO, K. & OTSUKA, N., Thermal and mechanical properties of aluminium titanate–mullite composites—1. Effects of composition. *Yogyo-kyokai-shi*, **94** (1986) 970–976.
13. YANO, T., NAGAI, N., KIYOHARA, M. & OTSUKA, N., Thermal and mechanical properties of aluminium titanate–mullite composites—2. Thermal shock resistance. *Yogyo-kyokai-shi*, **94** (1986) 1190–1192.
14. YANO, T., KIYOHARA, M. & OTSUKA, N., Thermal and mechanical properties of aluminium titanate–mullite composites—3. Effects of aluminium titanate particle size. *J. Ceram. Soc. Japan*, **100** (1992) 482–487.
15. MORISHIMA, H., KATO, Z., UEMATSU, K., SAITO, K., YANO, T. & OTSUKA, N., Synthesis of aluminium titanate–mullite composite having high thermal shock resistance. *J. Mater. Sci. Letters*, **6** (1987) 389–390.
16. KIM, J., ZOGRAFOU, C. & KRÖNRT, W., Thermal shock resistant materials based on aluminium titanate–mullite composites. In *Proceedings of the Unified International Technical Conference on Refractories* (Aachen, 1991), 2nd edn, ed. The German refractories association. Stahl und Eisen, 1992, pp.197–201.
17. WOHLFROMM, H., MOYA, J. S. & PENA, P., Thermal shock behaviour of aluminium titanate based materials. In *Proceedings of the Third European Ceramic Society Conference*, ed. P. Duran & J.F. Fernandez. Faenza Editrice lberica S.L., Spain,1993, pp.1003–1012.
18. HUANG, Y. X., SENOS, A. M. R. & BAPTISTA, J. L., Preparation of an aluminium titanate–25 vol% mullite composite by sintering of gel-coated powders. Submitted to *J. Eur. Ceram. Soc.*
19. FREUDENBERG, B. & MOCELLIN, A., Aluminium titanate formation by solid-state reaction of fine Al_2O_3 and TiO_2 powders. *J. Am. Ceram. Soc.*, **70** (1987) 33–38.
20. BUSCAGLIA, V., NANNI, P., BATTILANA, G., ALIPRANDI, G. & CARRY, C., Reaction sintering of aluminium titanate—II. Effect of different alumina powders. *J. Eur. Ceram. Soc.*, **13** (1994) 419–426.
21. LEQUEUX, N., BONHOMME-COURY, L., MUSSOTTE, S. & BOCH, P., Reaction sintering of ZrO_2-Al_2TiO_5 composites. In *Proceedings of the Third European Ceramic Society Conference*, ed. P. Duran & J.F. Fernandez. Faenza Editrice Iberica S.L., Spain, 1993, pp.1011–1016.
22. THOMAS, H. A., STEVENS, R. & GILBART, E., Effect of zirconia additions on the reaction sintering of aluminium titanate. *J. Mater. Sci.*, **26** (1991) 3613–3616.
23. HAMANO, K., NAKAGAWA, Z., SAWANO, K. & HASEGAWA, M., Effects of additives on several properties of aluminium titanate ceramic. *Chem. Soc. Japan*, **10** (1981) 1647–1655.
24. KAJIWARA, M., Sintering and properties of stablized aluminium titanate. *Br. Ceram. Trans. J.*, **86** (1987) 77–80.
25. PASK, J. A., ZHANG, X. W., TOMSIA, A. P. & YOLDAS, B. E., Effect of sol–gel mixing on mullite microstructure and phase equilibrium in the α-Al_2O_3–SiO_2 system. *J. Am. Ceram. Soc.*, **70** (1987) 704–707.
26. LEE, W. E. & RAINFORTH, W. M., *Ceramic Microstructures*. Chapman & Hall, London, 1994, pp. 299.
27. OHYA, Y., HAMANO, K. & NAKAGAWA, Z., Microstructure and mechanical strength of aluminium titanate ceramic prepared from synthesised powders. *Yogyo-Kyokai-Shi*, **91** (1983) 289–297.