Magnesium Aluminate Spinel Ceramics Containing Aluminum Titanate for Refractory Applications

K. Moritz[*], C.G. Aneziris, D. Hesky, N. Gerlach

Technische Universität Bergakademie Freiberg, Institute of Ceramics, Glass
and Construction Materials, Agricolastr. 17, 09596 Freiberg, Germany

Abstract

The thermal shock resistance of alumina-rich magnesium aluminate spinel refractory ceramics with aluminum titanate as second phase was investigated. First, suitable thermal conditions for the formation of aluminum titanate from corundum and rutile were determined. Ground pre-synthesized aluminum titanate was added to the spinel powder. According to another route, alumina and titania powder were mixed with the spinel raw material in order to form the aluminum titanate *in situ* during sintering. Test bars were prepared by means of slip casting and sintered at 1650 °C. The bending strength of both types of as-sintered samples with aluminum titanate was significantly lower in comparison with pure spinel ceramic, but their thermal shock resistance was improved. When the test bars were quenched five times from 950 or 1150 °C, the retained strength of the materials with aluminum titanate was higher than that of the pure spinel samples.

Keywords: Refractories, magnesium aluminate spinel, aluminum titanate, thermal shock resistance

I. Introduction

Magnesium aluminate spinel is an established material for refractory applications, for example in the steel industry, because of its suitable high-temperature properties such as high strength at elevated temperatures and high resistance to basic slags [1,2]. Besides the stoichiometric composition (71.8 wt% Al_2O_3, 28.2 wt% MgO), magnesia-rich and alumina-rich magnesium aluminate spinel materials exist [2]. Possible Al_2O_3 contents range from 65 to 90 wt% [3]. The spinel solid solution containing 90 wt% Al_2O_3 can be obtained at high temperatures up to 1900 °C and maintained by rapid cooling, but this spinel phase is thermodynamically unstable at steelmaking temperatures around 1600 °C. A mixture of spinel and corundum is formed. By contrast, alumina-rich spinel containing 78 wt% Al_2O_3, as used in the present work, remains stable at 1600 °C. The main aim of our research was to investigate the influence of aluminum titanate as second phase on the thermal shock resistance of magnesium aluminate spinel ceramics.

Aluminum titanate (tialite) ceramic itself is an excellent thermal-shock-resistant material [4]. Tialite is isomorphic with the mineral pseudobrookite. Owing to its low thermal expansion and low Young's modulus, aluminum titanate shows a high R_1 thermal shock parameter according to Hasselman, i.e. high resistance against crack initiation caused by thermal shock [5]. These characteristics can be explained by the anisotropy of thermal expansion within the tialite crystals leading to localized inter-

nal stresses and microcracking during cooling from the sintering temperature [6]. This is also responsible for the poor mechanical strength of tialite ceramic. In the temperature range from approximately 900 to 1280 °C, pure tialite undergoes decomposition into corundum and rutile. The decomposition rate depends on temperature, holding time, heating rate, phase purity, grain size, and atmosphere [7]. It is generally accepted that the maximum rate of Al_2TiO_5 decomposition can normally be found at around 1100 – 1150 °C [4,8]. Its instability in the mentioned temperature range is an essential drawback of pure aluminum titanate ceramic. Therefore, different oxidic additives such as MgO or Fe_2O_3 are used for stabilizing the titanate phase. Sintering of aluminum titanate with MgO or Fe_2O_3 additions results in the formation of pseudobrookite type solid solutions with the general formula $Al_{2(1-x)}Mg_xTi_{(1+x)}O_5$ and $Al_{2(1-x)}Fe_{2x}TiO_5$, respectively, showing an improved thermal stability in comparison with pure aluminum titanate [8–10]. Buscaglia *et al.* investigated the influence of MgO [11] or spinel ($MgAl_2O_4$) [12] additions on the titanate formation and microstructure evaluation by reaction sintering of corundum and rutile. When MgO is added, it reacts first with Al_2O_3 to $MgAl_2O_4$ at temperatures below 1100 °C. The authors assumed that the mechanism of titanate formation is influenced by $AlMg_{0.5}Ti_{1.5}O_5$ crystals, formed by reaction of $MgAl_2O_4$ with TiO_2 at temperatures above 1150 °C and acting as preferential sites for further titanate nucleation and growth. When the temperature is further increased, the composition of the solid solution approaches the final one. The resulting grain size is smaller than that of pure

---

[*] Corresponding author: Kirsten.Moritz@ikgb.tu-freiberg.de

aluminum titanate formed from the same powders and under the same conditions [11, 12].

Several publications describe the incorporation of aluminum titanate into an alumina matrix. Because its thermal expansion coefficients are extremely anisotropic and show large mismatch with alumina, aluminum titanate as second phase induces intense internal residual stresses improving the flaw resistance of the ceramic [13, 14]. The enhancement of the thermal shock resistance of fine-grained alumina with aluminum titanate is also reported [15, 16].

In a previous work of our group, so-called AZT ceramics were prepared from 95 wt% Al_2O_3-2.5 wt% ZrO_2-2.5 wt% TiO_2 powder mixtures. Following crystalline phases besides corundum were identified with X-ray diffraction after sintering: tialite, srilankite, and monoclinic zirconia. The tialite phase was found to be partially decomposed after quenching from 1200 °C [17, 18]. Both partial aluminum titanate decomposition and different thermal expansion coefficients of the crystalline phases present in the sintered material were assumed to contribute to the high thermal shock resistance of the AZT ceramics [17–19].

The thermal shock behavior of alumina-rich magnesium aluminate spinel ceramics containing an aluminum titanate phase is, as mentioned above, the topic of the present paper. The work is aimed at an application of the material for nozzles or nozzle inlay parts in steel casting.

II. Experimental

Following powders were used as raw materials: alumina-rich spinel AR 78 (fraction < 20 μm)/Almatis, alumina Martoxid® MR 70/Albemerle®, and titania Tronox® TR/Crenox. The $d_{50,3}$ values of the particle size distributions and the specific surface areas of these powders are listed in Table 1.

Table 1: Powder characteristics.

		$d_{50,3}$ value of the particle size distribution [μm]*	Specific surface area (BET) [m²/g]**
Alumina-rich magnesium aluminate spinel	AR 78 < 20 μm, Almatis	1.6	2.7
Alumina (corundum)	Martoxid® MR 70, Albemerle®, Martinswerk	0.8	6.8
Titania (rutile)	Tronox® TR, Crenox	1.9	5.2
* LS 230/Beckman Coulter ** AREAmeter II/Ströhlein Instruments			

(1) Aluminum titanate

First, suitable conditions for the synthesis of pure aluminum titanate by means of reaction sintering of Al_2O_3 Martoxid® MR 70 and TiO_2 Tronox® TR were determined. For this purpose, an aqueous suspension of an equimolar mixture of alumina and titania powder was prepared. The solids content of this suspension was 80 % by weight. The slurry contained ammonium polyacrylate as deflocculant, a binding agent on the basis of acrylate polymer, and a polysaccharide. It was homogenized in a rotating polyethylene container with alumina grinding balls for 24 h. Green bodies were prepared by means of slip casting in plaster moulds. The dimensions of the cavities of the moulds in which the samples were formed were approximately 5 × 4 × 50 mm³. After the organic additives had been burned out at 650 °C, the samples were heat-treated in air at the following temperatures and holding times: 1500 °C/2 h, 1650 °C/2 h, or 1650 °C/4 h. The heating rate was 1 K per minute. No cooling rate was given. The crystalline phases in the heat-treated samples, comminuted in a vibratory disc mill, were analyzed by means of X-ray diffraction (XRD) using the X'Pert PRO MPD 3040/60/PANalytical diffractometer with CuK$_\alpha$ radiation and the X'Pert HighScore software.

Based on the results, a temperature of 1650 °C and a holding time of 4 h were chosen for the synthesis of Al_2TiO_5.

For investigation of the thermal decomposition of aluminum titanate, Al_2TiO_5 samples produced in this way were heat-treated at two different temperatures in the decomposition range (1000 °C, 1150 °C). A heating rate of 1 K per minute and holding times between 2 and 24 h were used. The samples were left to cool in the furnace without a given cooling rate. XRD was used to determine the percentage of residual Al_2TiO_5. The microstructure of the heat-treated samples was investigated by means of scanning electron microscopy (XL-30 ESEM FEG/FEI) and elemental analysis with energy-dispersive X-ray spectroscopy (EDAX/AMETEK).

(2) Spinel with and without aluminum titanate

Spinel ceramics with aluminum titanate as second phase were prepared according to two different routes. According to the first route, pre-synthesized aluminum titanate samples were ground in a planetary ball mill (Pulverisette 5/Fritsch). 12 wt% of aluminum titanate and 88 wt% of the spinel powder were mixed. According to the second method, alumina and titania powder were added to the spinel powder in order to form the aluminum titanate *in situ* during sintering. The amounts of Al_2O_3 and TiO_2 corresponded to those needed for the formation of 12 wt% Al_2TiO_5. Pure spinel samples without aluminum titanate were produced for the purpose of comparison. All samples were fabricated as follows: Aqueous, 83 wt% solids content suspensions containing a carboxylic acid formulation as deflocculant and an acrylate polymer as binding agent were prepared and homogenized in rotating polyethylene containers with alumina grinding balls for 5 h. Longer homogenizing times were not used because they led to an increase in viscosity. Similar observations concerning the preparation of aqueous $MgAl_2O_4$ suspensions are also

described in the literature and are attributed to hydrolysis reactions causing coagulation [20]. Green bodies having the same dimensions as the Al_2O_3-TiO_2 samples for the Al_2TiO_5 synthesis were produced by means of slip casting. The organic additives were burnt out at 650 °C in air. Using pieces of the samples that were approx. 25 mm long, the change in length as a function of temperature in the range from 20 °C to the device-dependent upper limit of 1450 °C was measured at a heating rate of 5 K per min by means of a dilatometer DIL 402 C/Netzsch in order to compare the sintering behavior of the different spinel samples. The test bars for the thermal shock experiments were sintered in air at 1650 °C with 4 h holding time (heating rate: 1 K/min). For investigation of the thermal shock resistance, the sintered samples were exposed to a temperature of 950 or 1150 °C for 15 min and then quenched in water with a temperature of 25 °C. The strength of the as-sintered samples and the retained strength after one and five quenching cycles were measured in three-point bending tests in the TIRAtest 2420/TIRA testing machine.

Furthermore, the samples were investigated by means of X-ray diffraction and scanning electron microscopy using the equipment mentioned above.

III. Results and Discussion

(1) Synthesis and decomposition of pure aluminum titanate

Fig. 1 shows the percentage of Al_2TiO_5 formed by means of reaction sintering of the powders Al_2O_3 Martoxid® MR 70 and TiO_2 Tronox® TR at 1500 °C or 1650 °C. An aluminum titanate content of 90 wt% was obtained at 1500 °C and 2 h holding time. It could be increased up to 99 wt% when a temperature of 1650 °C was used.

Heat-treatment of aluminum titanate samples, synthesized at 1640 °C with 4 h holding time, at temperatures in the decomposition range resulted in partial or complete decomposition of Al_2TiO_5, depending on the temperature and dwell time. When the samples were exposed to a temperature of 1000 °C for 24 h, the content of residual Al_2TiO_5 was 56 wt%. By contrast, heat treatment at 1150 °C using the same holding time led to complete tialite decomposition. This is consistent with the temperature range of the maximum Al_2TiO_5 decomposition rate reported in the literature (see section I). The influence of the holding time on the degree of decomposition is shown in Fig. 2. A dwell time of 12 h was also sufficient for complete decomposition, but 6 wt% of residual aluminum titanate were found after 6 h and nearly 30 wt% after 2 h holding time.

As shown by the scanning electron micrographs in Figs. 3 and 4, fine grains of alumina and titania were formed within the former aluminum titanate grains during thermal decomposition. Based on elemental analysis with energy-dispersive X-ray spectroscopy (EDS), the dark grains can be attributed to Al_2O_3 and the light grains to TiO_2 (Fig. 4).
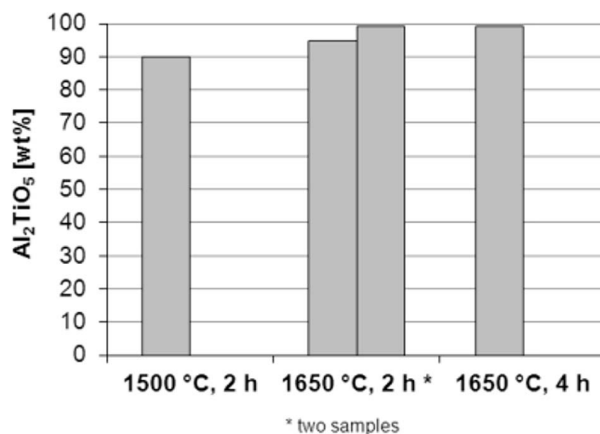

Fig. 1 : Percentage of aluminum titanate formed by reaction sintering of alumina and titania.
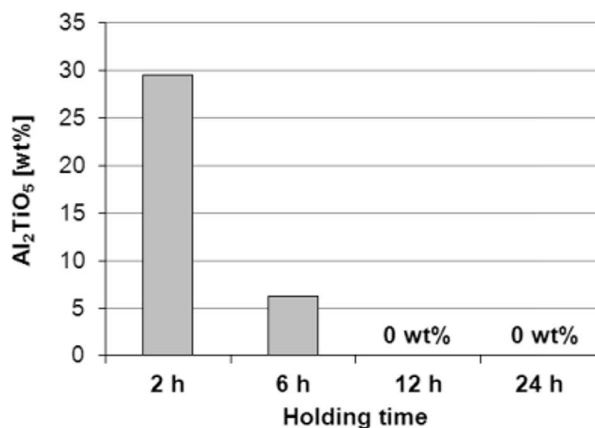

Fig. 2 : Influence of the holding time on the degree of aluminum titanate decomposition at 1150 °C: residual Al_2TiO_5 content.
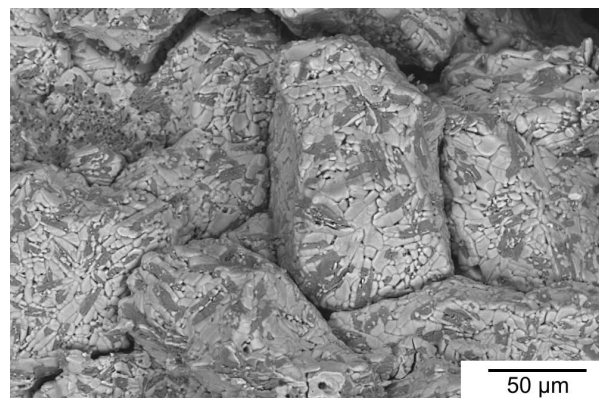

Fig. 3 : Scanning electron micrograph showing the fracture surface of a former aluminum titanate sample after Al_2TiO_5 decomposition at 1150 °C/24 h.

(2) Magnesium aluminate spinel containing aluminum titanate in comparison with pure spinel

The addition of pre-synthesized Al_2TiO_5 or Al_2O_3 and TiO_2 to alumina-rich magnesium aluminate spinel influenced the sintering behavior of the spinel samples as shown by their change in length as a function of temperature (Fig. 5). Compared with the pure spinel sample, densification of the sample containing pre-synthesized Al_2TiO_5 started at lower temperatures. The temperature at which sintering began was further reduced with the addition of Al_2O_3 and TiO_2 instead of pre-synthesized Al_2TiO_5. The knee in the shrinking curve indicates the onset of Al_2TiO_5 formation. Because of the lower density of aluminum ti-

tanate in comparison with the starting materials, its formation based on solid state reaction of alumina and titania is accompanied by an increase in volume. The onset of densification at lower temperatures can be attributed to the effect of TiO_2. Titania is known to promote sintering of alumina [21] and reaction sintering of magnesium aluminate spinel [22]. As can be seen in Fig. 6, sintering at 1650 °C resulted in significantly larger grains of the ceramics with pre-synthesized or *in situ*-formed aluminum titanate in comparison with the pure spinel samples.
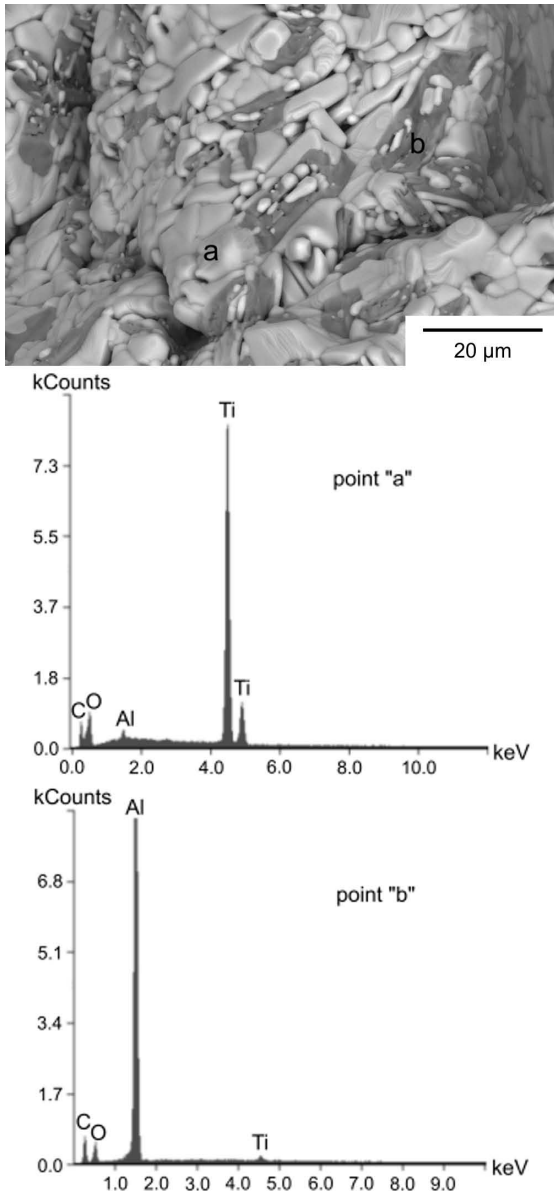
Fig. 4: EDS elemental analysis of the grains formed by decomposition of aluminium titanate.

The strength of the as-sintered samples with aluminum titanate was significantly lower than that of the as-sintered pure spinel ceramic (Fig. 7a). In all cases, quenching caused a decrease in strength (Fig. 7b). The bending strength of the pure spinel ceramic decreased by nearly 90 % from 122.5 MPa after sintering to approximately 12.8 MPa after the first quenching from 950 °C. By contrast, the strength of the ceramic containing 12 wt% presynthesized aluminum titanate was 13.3 MPa after sintering and decreased by 12.8 % to 11.6 MPa when the samples

were first quenched from 950 °C. Note that the difference between the initial and retained strength was in the range of error in this case. The strength of the as-sintered samples with *in situ*-formed aluminum titanate was 25.6 MPa. First quenching from 950 °C resulted in a decrease by 34.8 % to 16.7 MPa. A larger drop in strength was observed in all cases when the samples were quenched from 1150 °C.
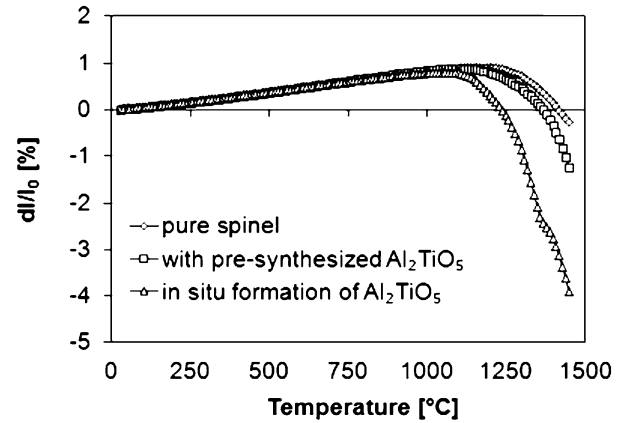

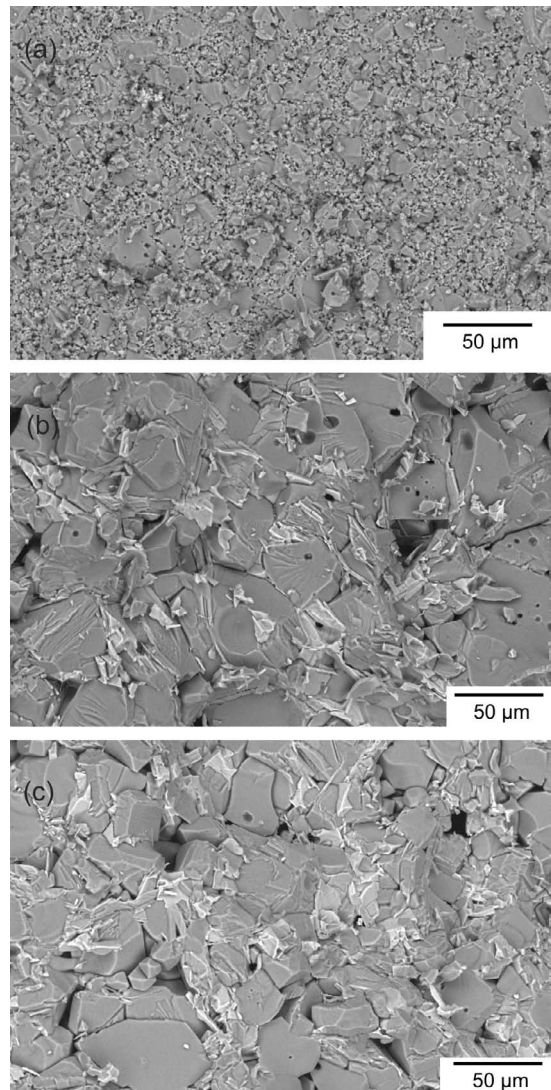**Fig. 5:** Change in length of spinel samples as a function of temperature.

Fig. 6: Scanning electron micrographs showing the fracture surface of as-sintered spinel samples: a) without aluminum titanate; b) with pre-synthesized aluminum titanate; c) with *in-situ*-formed aluminum titanate.
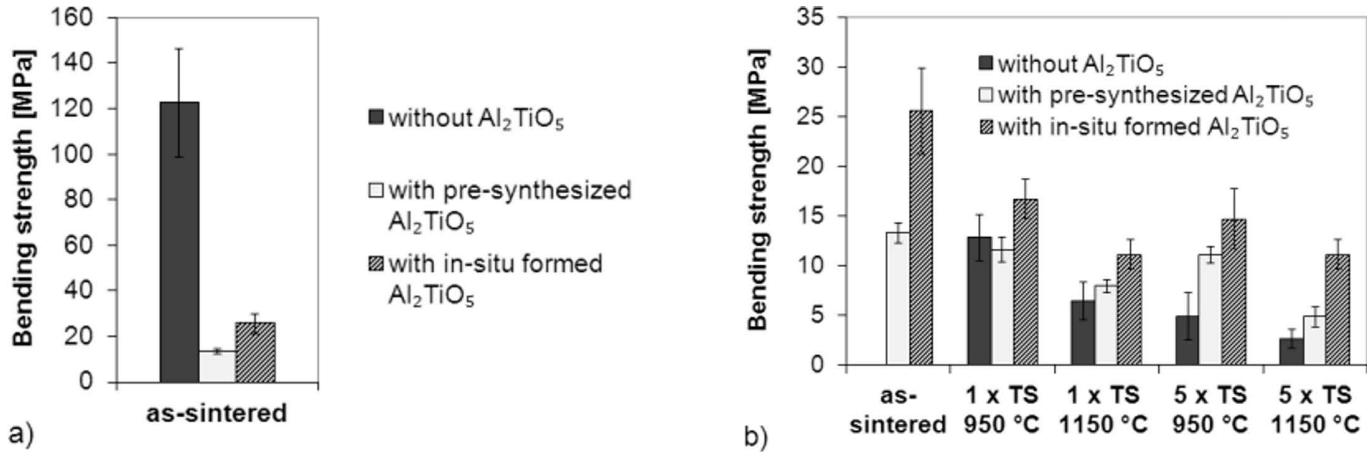
Fig. 7 : Bending strength of spinel samples with and without aluminum titanate: a) after sintering and; b) after thermal shock (TS) by quenching from 950 °C and 1150 °C.

Compared with the pure spinel ceramic, both materials with aluminum titanate showed a higher retained strength after the fifth quenching from 950 or 1150 °C. The ceramic containing *in situ*-formed aluminum titanate had the highest residual strength after repeated thermal shock.

Figs. 9a and b show X-ray diffractograms of spinel samples with pre-synthesized or *in situ*-formed aluminum titanate after sintering and after the first and fifth quenching from 1150 °C. The diffractograms of pre-synthesized aluminum titanate (Al_2TiO_5 content: 99 wt%) and of an as-sintered pure spinel sample are given for comparison (Fig. 8). The diffraction peaks which can be attributed to aluminum titanate are marked in Fig. 9 with an asterisk, the spinel peaks are marked with a circle. There was no significant decomposition of the titanate phase during the thermal shock experiments. The Al_2TiO_5 diffraction peaks did not diminish in intensity, except for a slight decrease after the fifth quenching of the ceramic with *in situ*-formed aluminum titanate.
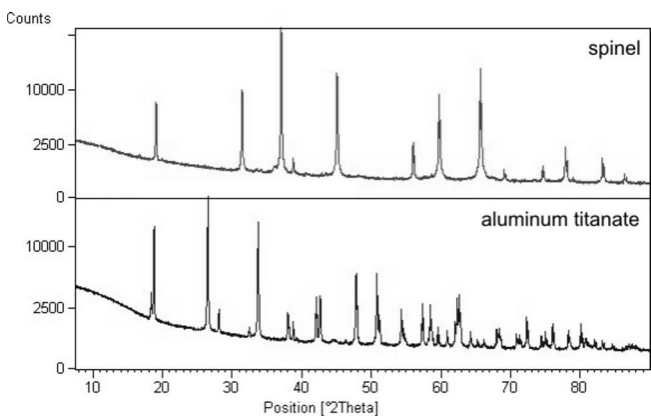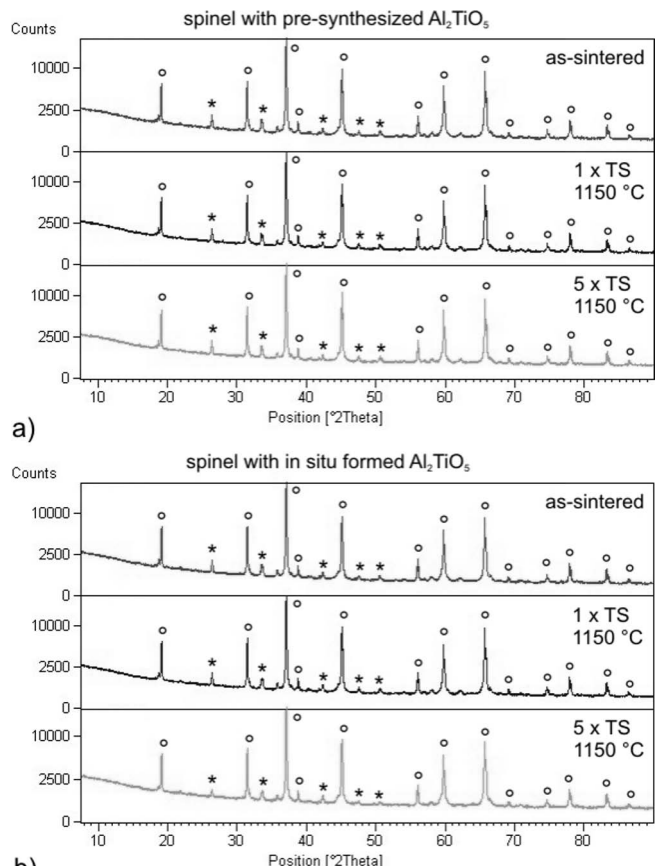

a)

b)

Fig. 9 : X-ray diffractograms of spinel ceramic: a) with pre-synthesized aluminum titanate; b) with *in-situ*-formed aluminum titanate; (° spinel, * aluminum titanate).

IV. Summary

Alumina-rich magnesium aluminate spinel ceramics with aluminum titanate as second phase were produced according to two different routes: with the addition of pre-synthesized Al_2TiO_5 to the spinel powder or the addition of Al_2O_3 and TiO_2 powder in order to form Al_2TiO_5 *in situ* during sintering. Samples were prepared by means of slip-casting and sintered at 1650 °C. Al_2TiO_5 or Al_2O_3

Fig. 8 : X-ray diffractograms of an as-sintered pure spinel sample and of aluminum titanate formed by reaction sintering.

and TiO_2 promoted sintering and grain growth, attributed to titania acting as a sintering aid. In comparison with the as-sintered pure spinel ceramic, the strength of the Al_2TiO_5-containing samples after sintering was drastically reduced, and the relative change in strength caused by quenching from 950 or 1150 °C was lower. The retained strength after five quenching cycles was higher than that of the pure spinel samples. The ceramics with aluminum titanate showed an improved thermal shock resistance.

Acknowledgement

References

[1] Sarkar, R.: Refractory applications of magnesium aluminate spinel, *Interceram: Refractories Manual*, 11 – 15, (2010).

[2] Racher, R.P., McConnell, R.W., Buhr, A.: Magnesium aluminate spinel raw materials for high performance refractories for steel ladles, www.almatis.com/download/technicalpapers, n.d.

[3] Bartha, P.: Magnesia spinel and spinel bricks (in German). In: Taschenbuch Feuerfeste Werkstoffe (Handbook of Refractories). Routschka, G. (Ed.). Vulkan-Verlag, Essen, Germany, 1997.

[4] Low, I.M., Oo, Z.: Reformation of phase composition in decomposed aluminum titanate, *Mater. Chem. Phys.*, **111**, 9 – 12, (2008).

[5] Aneziris, C.G., Pfaff, E.E., Maier, H.R.: Ceramic materials in the system ZrO_2-TiO_2-Al_2O_3 for applications in the ferrous and non-ferrous metallurgy, *Key Eng. Mater.*, **136**, 1829 – 1833, (1997).

[6] Ohya, Y., Nakagawa, Z., Hamano, K.: Grain boundary microcracking due to thermal expansion anisotropy in aluminum titanate ceramics, *J. Am. Ceram. Soc.*, **70**, C185 – C186, (1987).

[7] Low, I.M., Lawrence, D., Smith, R.I.: Factors controlling the thermal stability of aluminum titanate ceramics in vacuum, *J. Am. Ceram. Soc.*, **88**, 2957 – 2961, (2005).

[8] Buscaglia, V., Nanni, P.: Decomposition of Al_2TiO_5 and $Al_{2(1-x)}Mg_xTi_{(1+x)}O_5$ ceramics, *J. Am. Ceram. Soc.*, **81**, 2645 – 2653, (1998).

[9] Ishitsuka, M., Sato, T., Ebdo, T., Shimada, M.: Synthesis and thermal stability of aluminum titanate solid solutions, *J. Am. Ceram. Soc.*, **70**, 69 – 71, (1987).

[10] Tilloca, G.: Thermal stabilization of aluminum titanate and properties of aluminum titanate solid solutions, *J. Mater. Sci.*, **26**, 2809 – 2814, (1991).

[11] Buscaglia, V., Nanni, P., Battilana, G., Aliprandi, G., Carry, C.: Reaction sintering of aluminum titanate: I – effect of MgO addition, *J. Eur. Ceram. Soc.*, **13**, 411 – 417, (1994).

[12] Buscaglia, V., Alvazzi Delfrate, M., Leoni, M., Bottino, C., Nanni, P.: The effect of $MgAl_2O_4$ on the formation kinetics of Al_2TiO_5 from Al_2O_3 and TiO_2 fine powders, *J. Mater. Sci.*, **31**, 1715 – 1724, (1996).

[13] Runyan, J.L., Bennison, S.J.: Fabrication of flaw-tolerant aluminum-titanate-reinforced alumina, *J. Eur. Ceram. Soc.*, **7**, 93 – 99, (1991).

[14] Padture, N.P., Bennison, S.J., Chan, H.M.: Flaw-tolerance and crack-resistance properties of alumina-aluminum titanate composites with tailored microstructures, *J. Am. Ceram. Soc.*, **76**, 2312 – 2320 (1993)

[15] Uribe, R., Baudin, C.: Influence of a dispersion of aluminum titanate particles of controlled size on the thermal shock resistance of alumina, *J.Am. Ceram. Soc.*, **86**, 846 – 850, (2003).

[16] Bueno, S., Berger, M.H., Moreno, R., Baudin, C.: Fracture behaviour of microcrack-free alumina-aluminum titanate ceramics with second phase nanoparticles at alumina grain boundaries, *J. Eur. Ceram. Soc.*, **28**, 1961 – 1971, (2008).

[17] Aneziris, C.G., Dudczig, S., Gerlach, N., Berek, H., Veres, D.: Thermal shock performance of fine-grained Al_2O_3 ceramics with TiO_2 and ZrO_2 additions for refractory applications, *Adv. Eng. Mater.*, **12**, 478 – 485, (2010).

[18] Dudczig, S., Veres, D., Aneziris, C.D., Skiera, E., Steinbrech, R.W.: Nano- and micrometre additions of SiO_2, ZrO_2 and TiO_2 in fine grained alumina refractory ceramics for improved thermal shock performance, *Ceram. Int.*, **38**, 2011 – 2019, (2011).

[19] Aneziris, C.G., Schärfl, W., Ullrich, B.: Microstructure evaluation of Al_2O_3 ceramics with Mg-PSZ- and TiO_2-additions, *J. Eur. Ceram. Soc.*, **27**, 3191 – 3199, (2007).

[20] Ganesh, I.: Aqueous slip casting of $MgAl_2O_4$ spinel powder, *Bull. Mater. Sci.*, **34**, 327 – 335, (2011).

[21] Sathiyakumar, M., Gnanam, F.D.: Influence of MnO and TiO_2 additives on density, microstructure and mechanical properties of Al_2O_3, *Ceram. Int.*, **28**, 195 – 200, (2002).

[22] Sarkar, R., Bannerjee, G.: Effect of TiO_2 on reaction sintered MgO-Al_2O_3 spinels, *J. Eur. Ceram. Soc.*, **20**, 2133 – 2141, (2000).