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Further tailoring of material properties in non-equimolar aluminium titanate ceramic materials

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Abstract

The authors started their R&D activities related to aluminium titanate (AT) ceramics in the early 1990s by addressing the critical problems of aluminium titanate, such as thermodynamical instability and micro-cracking. After that, their focus has permanently been on improving, optimizing and tailoring the properties of the aluminium titanate ceramic materials produced by reaction-sintering of *equimolar* mixtures of alumina and titania powders. This paper presents their latest investigations on AT ceramics produced by reaction-sintering of *non-equimolar* mixtures of the two main components. The objective of these investigations has been to emphasize the effects of excesses of either alumina or titania on the internal stresses build up in these materials and the consequences these internal stresses could have on some material properties which are most important for the industrial applications of AT ceramics. The ways and the extent in which these internal stresses could be controlled/managed were investigated, with the ultimate goal of expanding the possibilities for further tailoring the thermo-mechanical properties of the aluminium titanate ceramics, so that they meet specific application requirements.

Keywords: Non-equimolar; Al_2TiO_5; Powders-solid state reaction; Strength; Structural applications

1. Introduction

Rojan Advanced Ceramics, based in Perth, Western Australia, has been involved in R&D activities related to aluminium titanate for more than a decade and currently produces a wide range of AT materials and products which are exported throughout the world, mainly for applications in the non-ferrous metallurgy.

Whole families of aluminium titanate ceramic materials were developed, based on compositions containing *equimolar* ratios of Al_2O_3 and TiO_2. Small amounts of various additives were also used with the aim of improving the thermodynamic stability at intermediate temperatures.

Aluminium titanate has inherently a relatively low mechanical strength. Although the AT strength is higher than that of some competing materials, such as calcium silicate and fused silica, this strength is much lower than that of another main competitor, sialon.

AT has still some advantages over sialon, as it is much cheaper and a much better thermal insulator. However, any increase in the strength of AT is more than welcome.

As a consequence of a pronounced thermal expansion anisotropy, intergranular micro-cracking can occur in aluminium titanate. This can decrease the strength of the material on one side, and increase its toughness (and thermal shock resistance) on the other.

The authors found previously that, for average grain sizes around, or slightly above the critical grain size for intergranular micro-cracking, both a reasonably good strength and a substantial gain in toughness can be achieved.

According to these findings, a trade is possible between these antagonistic parameters, and specific AT materials with properties tailored to suite particular applications can be developed within each of the families mentioned above.[1]

Further developments at Rojan were able to achieve increases in the strength of our AT ceramics of up to 2.5 times, without a penalty on the thermal shock resistance. This was attained by refining the powder processing and ceramic forming technologies, and, finally, by optimizing the firing programs. In addition, a ceramic composite material based on aluminium titanate was also developed with a mechanical strength five times higher than the common AT material.[2]

This paper is presenting the results of a recent short-term R&D programme, which has investigated *the effects of deviations from the equimolar* composition of aluminium titanate on

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the material properties that are most relevant for the industrial applications of AT ceramics. Some preliminary results were previously reported.[3]

2. Experimental

Samples of non-equimolar AT compositions with either alumina or titania excesses ranging from 0% to 100% were investigated. Two series of water-based slurries were prepared by using alumina and titania powder mixtures with 0%, 5%, 15%, 30%, 50%, 75% and 100% alumina, respectively titania excess. Stabilizing additives were also used in the same amounts as for the equimolar AT.

Several prismatic blocks 40 mm × 40 mm × 100 mm were pressure-cast from each slurry, and then let to dry at room temperature for about 1 week.

A first complete series of 14 blocks was then fired with a dwell of 4 h at 1400 °C. Because some blocks with higher component excesses sintered under these conditions developed heavy cracks and, in the worst case, even disintegrated, repeat firings were performed on identical spare blocks with dwells of 6, 8 and even 10 h at 1400 °C, until the sintered blocks remained intact.

Two other complete series of 14 prismatic blocks were subsequently fired to 1450 and 1500 °C, respectively, with dwell times of 4 h. All sintered blocks, irrespective of the level of component imbalance, remained intact this time.

The sintered prismatic blocks had first the dense and hard skin ground off, in order to expose the bulk of the material. They were then cut into samples that were used for material property investigations. About 10 MoR bars, as well as samples for XRD and SEM analyses were prepared from each of these blocks.

Density and porosity were measured by Archimedes' method according to the Australian Standard AS 1774.5-1989, by following the evacuation procedure.

The XRD investigations have been performed at Curtin University of Technology in Perth, Western Australia, with a Siemens D500 diffractometer, by using the Cu Kα radiation, and they are still continuing.

The SEM samples were prepared at Rojan. They were polished with diamond grits going down to 0.25 μm average particle size, by using a Kent 3 automatic lapping and polishing machine manufactured by Kemet International. The polishing process was checked by using a Kyowa (Tokyo, Japan) optical microscope. The SEM examinations, including EDAX analyses, have been performed at the University of Western Australia in Perth, with a Philips 505 scanning electron microscope, and they are still continuing.

The modulus of rupture (MoR) was measured in four-point bending tests at Rojan, by using an X-Tran machine and load cell, while the rupture load was registered by an Ozy-Dyn apparatus. The dimensions of the MoR bars were 3 mm × 4 mm × 50 mm. The distance between the upper load points was 7 mm, while the lower load points were 20 mm apart. The width and thickness of the bar at the rupture point were measured with digital callipers, with an accuracy of 0.01 mm.

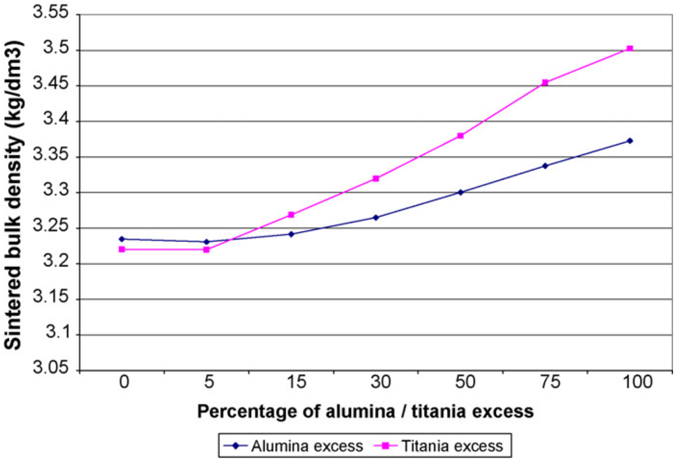

Fig. 1. Sintered bulk density vs. alumina/titania excess.

Eight to ten MoR bars were prepared from each non-equimolar AT material variety. Each MoR bar was then subjected to two consecutive four-point bending tests. The average of the 16–20 measured values was used in the strength versus component excess and sintering temperature graphs.

3. Results and discussion

The density and porosity values showed gradual variations with the alumina, respectively titania excess (see Figs. 1–3, for samples fired at 1450 °C/4 h; the theoretical density of the equimolar aluminium titanate is $D_T = 3.68$ kg/dm^3).

Some preliminary XRD results were presented elsewhere.[4] The results obtained so far show first some gradual changes in the lattice parameters with increasing component excesses. Then, for higher excesses, they indicate the presence of secondary phases formed by the component in excess. The complete results of the XRD investigations will make the object of a future report.

SEM results showed that the 1400 °C/4 h sintering resulted in AT grain sizes between 1 and 4 μm and no micro-cracks. The 1450 °C/4 h sintering produced AT grains of 3–6 μm size and only occasional intergranular micro-cracking. After sintering at

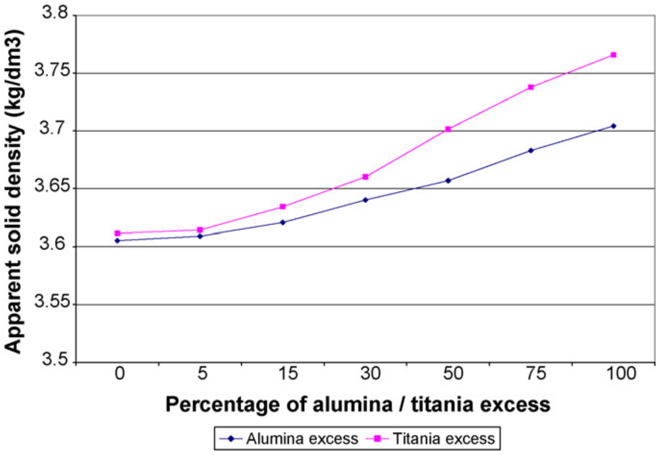

Fig. 2. Apparent solid density vs. alumina/titania excess.

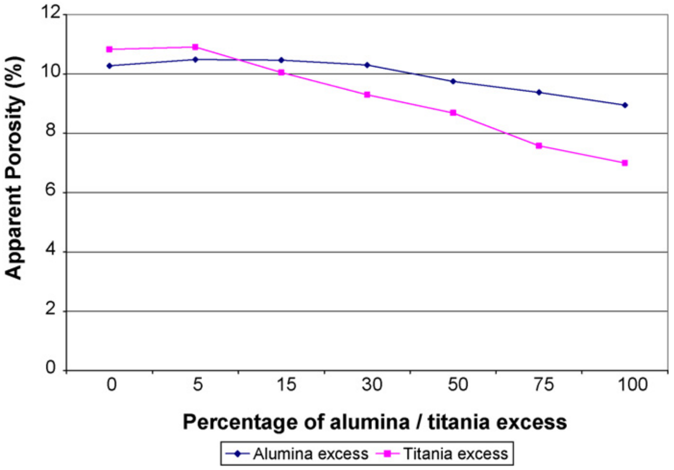

Fig. 3. Apparent (open) porosity vs. alumina/titania excess.

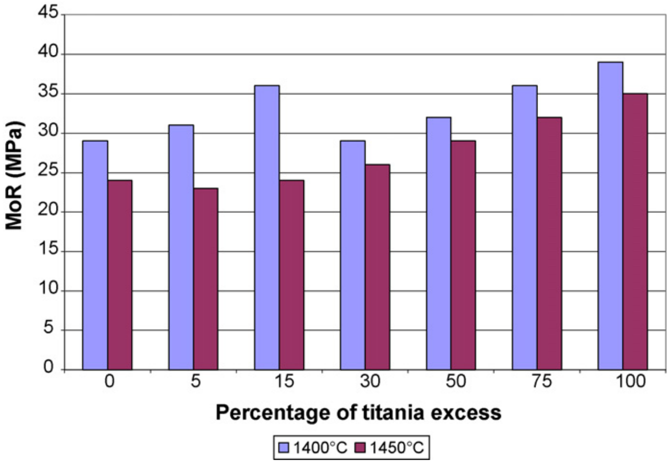

Fig. 5. Flexural strength vs. titania excess.

1500 °C for 4 h, the AT grain size was 5–10 μm and micro-crack free domains of 40–50 μm were surrounded by pronounced intergranular, and sometimes, trans-granular micro-cracks. Secondary phases were apparent in samples with high component excesses. The complete results of the SEM investigations will make the object of a separate report.

The MoR results showed a general tendency of increase in the four-point bending strength of the non-equimolar aluminium titanate materials with increasing alumina and titania excesses (see Figs. 4 and 5).

Fig. 4 presents a chart showing the variation of the bending strength with the amount of alumina excess. The row of darker columns represents the results for samples sintered at 1450 °C for 4 h and shows a monotonous increase of the material strength with increasing alumina excess.

The row of lighter columns in Fig. 4 represents the results of the 1400 °C firings. The data for samples no. 1 (zero alumina excess) to no. 5 (50% alumina excess) represent the results obtained for the 1400 °C/4 h sintering and show an increasingly pronounced tendency towards large increases in strength with increasing alumina excess.

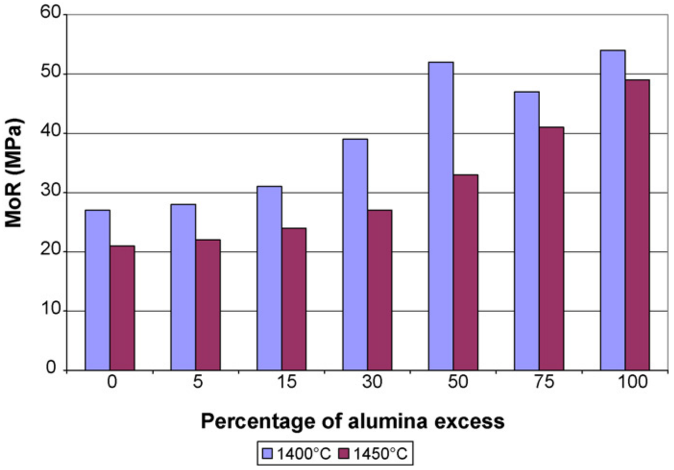

Fig. 4. Flexural strength vs. alumina excess.

The corresponding samples with 75% and 100% alumina excess were heavily cracked after being sintered at 1400 °C for 4 h only, so that it was not possible to measure their strength. The data represented on the same row of the graph in Fig. 4 for samples no. 6 and no. 7 were obtained on repeat samples which were sintered at the same temperature, 1400 °C, but for 6 and 8 h, respectively.

Fig. 5 shows a chart representing the variation of the bending strength with the amount of titania excess. Again, the row of darker columns represents the results on samples sintered at 1450 °C for 4 h, and shows a gradual increase in strength with increasing titania excesses.

Once again, the other row of columns in the graph in Fig. 5 represents the results obtained on samples sintered at 1400 °C. The data for the first three samples (with 0%, 5% and 15% titania excess) were obtained after a sintering at 1400 °C for 4 h and show a pronounced tendency towards significant increases in strength with increasing titania excess.

The other samples with larger titania excesses did not allow any measurement of their strength, as they were heavily distorted and cracked. After sintering at 1400 °C for 1 h only, a repeat sample with 100% titania excess has kept exfoliating and hurling small chips meters away for several days, whilst sitting on a laboratory bench, until a small, heavily cracked, egg-shaped core was left.

The data represented in the row of lighter columns on the graph in Fig. 5 for samples no. 4 to no.7 were obtained on repeat samples, which were sintered again at 1400 °C, but for 6 h (samples no. 4 and no. 5), 8 h (sample no. 6) and even 10 h (sample no. 7) in order to preserve their integrity.

It became clear that with increasing alumina/titania excess, larger and larger internal stresses can accumulate and remain preserved within these materials, leading in some cases to formation of large individual cracks and, in the worst cases, to the complete destruction of the test pieces.

Aluminium titanate is an "artificial" material that is synthetised at high temperature (≥1300 °C) by the direct reaction of alumina and titania. It is worth stressing here that during the AT forming reaction a volume expansion of about 10.7%

takes place. This goes against the volume shrinkage (∼35%) associated with sintering. The competition of these two antagonistic processes leads to development of internal stresses in the reaction-sintered aluminium titanate.

There is yet another prominent cause for internal stresses being built up in the reaction-sintered aluminium titanate. Both alumina and titania start sintering at temperatures lower than the ∼1300 °C threshold for aluminium titanate reaction of formation. That means that some degrees of sintering take place within the two main components, alumina and titania, before the reaction of AT formation takes off. The volume increase due to this reaction is thus constrained by the rigid structures of the partly sintered components.

Another series of sintering experiments was performed on equimolar alumina and titania mixtures, in which two different ramp rates were used between 1000 and 1300 °C:

- *low rate*: 150 °C/h, which would allow some sintering of the components;
- *high rate*: 300 °C/h, aimed at less sintering of the components prior to the onset of the AT forming reaction.

The low rate sintering experiments systematically delivered AT materials with higher strength values, in agreement with our expectations.

This effect will be amplified if there is a significant compositional imbalance of the two main components, i.e. when there is a large excess of either alumina or titania. Titania starts sintering at lower temperatures than alumina and that is why this effect is more pronounced in high titania excess, reaction-sintered AT.

Such internal stresses, if preserved within the sintered material, will have on one hand a hardening effect, with a possible increase in mechanical strength. On the other hand, there will certainly be an increased brittleness and a higher probability of cracks and failure.

In order to avoid the preservation of high internal stresses some measures had to be taken that would promote stress relaxation. This was attempted in repeat sintering experiments for samples with large alumina/titania excesses, by either providing for longer dwell times for sintering at lower temperatures (1400 °C), or, alternatively, by using a higher sintering temperature (1450 or 1500 °C).

Increased sintering times seemed to allow a significant stress relaxation, so that samples with high alumina/titania excesses were no longer subject to cracking. However, as expected, the strength of these samples was somewhat diminished. Similar changes were obtained when sintering was performed at higher temperatures (see Figs. 4 and 5).

Some studies (see, e.g. Segadaes et al.[5]) showed that a compositional imbalance, specifically an alumina excess, can accelerate the decomposition of AT. The explanation offered by some authors was that the excess alumina acts as nucleation centres for the reaction of decomposition.

This is, most probably, true. But the driving force for decomposition in such cases is related, in our opinion, to the internal stresses caused by the compositional imbalance, as explained here above. When no or not enough stress relaxation is provided, these internal stresses remain preserved within the reaction-sintered AT material, and there will be a natural tendency for it to decompose and thus eliminate the stresses and minimize the internal energy of the system. Alternatively, when an effective relaxation of the internal stresses takes place during the reaction-sintering cycle, a more thermodynamically stable aluminium titanate should result.

Our interpretation is also consistent with early studies, which showed that higher sintering temperatures and longer dwell times yielded thermodynamically more stable AT materials.[6]

4. Conclusion

These studies open the way for further possibilities of tailoring the aluminium titanate ceramic materials according to requirements of specific applications. Again there is a trade possible between higher strength on one side and higher toughness (and thermal shock resistance) on the other, as well as between higher strength on one side and higher thermodynamic stability on the other.

References

1. Alecu, I. D. and Stead, R. J., Aluminium titanate ceramics—an attractive solution. In *Proceedings of the 30th Internat. Symp. on Automotive Technology and Auto-motion, ISATA'97, Paper 97NM061*, June 1997.
2. Alecu, I. D., Cilia, R. A., Dean, G. A., Reuben, R., Stead, R. J. and Wing, R. F., New developments in aluminium titanate ceramics and refractories. In *Proceedings of the Seventh ECerS Conference, Key Engineering Materials, vols. 206–213*, 2002, pp. 1705–1710.
3. Alecu, I. D. and Stead, R. J., Non-equimolar aluminium titanate. In *Proceedings of the Australasian Ceram. Soc. Conf., AUSTCERAM 2004*, December 2004.
4. Alecu, I. D., Stead, R. J. and Hart, R. D., XRD investigations on non-equimolar aluminium titanate. In *Proceedings of the Australasian Ceram. Soc. Conf., AUSTCERAM 2004*, December 2004.
5. Segadaes, A. M., Morelli, M. R. and Kiminami, R. G. A., Combustion synthesis of aluminium titanate. *J. Eur. Ceram. Soc.*, 1998, **18**, 771–781.
6. Thomas, H. A. J. and Stevens, R., Aluminium titanate—a literature review. Part 2. Engineering properties and thermal stability. *Br. Ceram. Trans. J.*, 1989, **88**(4), 184–190.