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Aluminium Titanate Sintering Study Aimed at Rational Design of Microstructure for Optimal Thermal Shock Characteristics

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Aluminium titanate is highly anisotropic in thermal expansion. As a result, thermal stresses build up in the material and intergranular cracks can develop. Both the outstanding thermal shock resistance and the low mechanical strength of aluminium titanate ceramics are a result of intergranular microcracking. The authors have previously identified a possibility of remarkably increasing fracture toughness of aluminium titanate without excessive penalty on strength. The paper shows that sintered density and porosity measurements can be used for optimizing the sintering and microstructure of aluminium titanate for an ideal balance between toughness and strength and, hence, the best thermal shock resistance.

Key words : Microcracking, Density, Porosity, Thermal shock

I. Introduction

There is currently a world wide strong resurgence of the interest in aluminium titanate (Al_2TiO_5) ceramic materials triggered by their set of outstanding properties, their applicability in many modern industry branches, such as the automotive industry or the non-ferrous metallurgy, and by recent advances in technology.

Some of the remarkable properties of aluminium titanate (AT) are[1]:

* relatively high melting point (1860°C)
* very low thermal expansion coefficient
* low Youngs modulus
* exceptional thermal shock resistance
* low porosity and gas/liquid permeability
* very good thermal insulating characteristics
* very good phonic insulating properties
* non-wettable and non-reactive with molten non-ferrous metals and alloys
* easily machinable, even in sintered state.

However, we must mention that most of these properties are not intrinsic material characteristics. They are actually consequences of intergranular microcracking.

The AT crystals have a pronounced anisotropy in thermal expansion which usually results in intergranular mismatch stresses and possibly in generalized intergranular microcracking during cooling down from the firing temperature.[2]

The thermal expansion coefficients along the three crystallographic axes determined from X-ray diffraction data are[3,4]:

$\alpha_a \cong 20\times10^{-6}K^{-1}$, $\alpha_b \cong 10\times10^{-6}K^{-1}$, $\alpha_c \cong -3\times10^{-6}K^{-1}$

The development of microcracks most commonly occurs during cooling, normal to directions of high contraction (a-axes), due to the development of tensile stresses when grains are bonded in such directions.

Microcrack formation cancels the tensile stresses developed during cooling. In addition, the microcracks along the grain boundaries provide some sort of "cushion" into which adjacent grains may expand freely when the temperature is increased. The quoted very low bulk thermal expansion coefficient is thus not an intrinsic property of the material, but a consequence of the intergranular microcracking processes.

The formation of microcracks is not solely dependent on the thermal expansion anisotropy, but is also strongly influenced by the grain size of the material. Studies have shown that in such anisotropic materials as aluminium titanate there is a critical grain size above which only microcracking occurs.[5,6]

Earlier work done at Rojan Advanced Ceramics showed that by using substitutional additives and controlling the grain size it was possible to overcome the decomposition problem and also master the microcracking problems encountered with aluminium titanate ceramics.[7,8]

Due to the determinant role of the intergranular microcracking on the material properties of AT ceramics, the control of microcracking proved to be the most important key to a successful tailoring of these ceramics for various applications.

According to an idealised model, for grain sizes smaller than the critical grain size for microcracking, no intergranular microcracking would occur, with consequences such as: high mechanical strength, low work of fracture (i.e. brittleness).

For grain sizes equal to or greater than the critical

grain size for microcracking generalised intergranular microcracking would occur, with opposite consequences such as: low mechanical strength, high work of fracture (i.e. toughness).

However, such an abrupt change in properties at a sharply defined critical grain size can only be imagined in a ceramic material with a very narrow grain size distribution.

Otherwise, a substantial gain in fracture toughness and a reasonably good strength can be expected for average grain sizes around or slightly above the critical value for intergranular microcracking. Such a possibility was thoroughly investigated and very well documented by Evans and Fu[9] for other ceramic materials.

The increase in fracture toughness would be due to an ability to generate under such circumstances **discrete** intergranular microcracks, within a "reaction zone" ahead of the advancing crack, which would absorb energy and thus induce crack shielding.

II. Experimental Procedure

Aluminium titanate samples including small tablets (25 mm diameter × 5 mm height) and MoR (Modulus of Rupture) rectangular bars (3 mm high × 4 mm wide × 50 mm long) were prepared by the ceramic forming technique called slip casting.

Mixtures of high purity corundum alumina, rutile titania and additive (such as MgO) powders were used to prepare stable suspensions in demineralised and deionised water.

Hydrochloric acid or ammonium polyacrylate were used as dispersant/defloculant. Good castable slips with solids contents of 65 to 75 wt% and viscosities of 100 to 800 mPa.s were obtained at pH values around 3 or 10.

Samples were produced by solid casting in Plaster of Paris moulds. They were let to dry for 48 hours at the ambient temperature, then subjected to a so called low-fire cycle in order to eliminate any traces of water and organic additives. Finally, the AT samples were sintered in air at temperatures ranging from 1300 to 1600°C, with dwell times of 1 to 4 hours.

The sintered samples were then subjected to various examinations and investigations in order to determine some of the most relevant material characteristics:

* phase composition (by XRD analyses)
* microstructural features (by SEM examinations)
* density and porosity (by Archimedes method)
* coefficient of thermal expansion (by dilatometry)
* flexural strength, MoR (by 4 point bending tests)
* thermal shock resistance (MoR after water quenching tests).

III. Results and Discussion

The results of the XRD examinations showed that all our samples were beta aluminium titanate, with a few of them displaying also some very weak corundum and/or rutile peaks.

SEM examinations were performed on three samples of aluminium titanate sintered for 4 hours at 1300, 1400, and 1450°C respectively. The sample sintered at 1300°C had grain sizes between 1 and 3 μm and no intergranular microcracking was visible. The second AT sample, sintered at 1400°C, had grain sizes in the range 2 to 5 μm and, again, no intergranular microcracks could be observed. Finally, the sample sintered at 1450°C had grain sizes between 4 and 8 μm, and commonly domains of 20 to 50 μm free of intergranular microcracks were formed, separated among them by pronounced intergranular and, sometimes, transgranular microcracks.

Dilatometry investigations were performed on two aluminium titanate samples, one with an average grain size of about 4 μm, sintered at 1400°C, and the other with an average grain size of about 12 μm, sintered at 1550°C. Both of them were subjected to successive heating and cooling cycles with increasing top temperatures.

When cycled up to 500, 700 and 900°C and back to room temperature, the 4 μm sample showed negligible thermal expansion up to only 150-200°C, then expanded quite significantly, with an expansion coefficient close to the average value $(\alpha_a+\alpha_b+\alpha_c)/3$ expected for a non-textured polycrystalline aluminium titanate ($\alpha \cong 10 \times 10^{-6}$ K^{-1}).

Only when cycled up to 1100, 1300 and 1500°C and back to room temperature this sample exhibited negligible thermal expansion up to about 600-700°C, then high expansion up to the respective top temperature.

These results are consistent with the hypothesis that the 4 μm average grain size material had initially an insignificant level of microcracking, and only after thermally cycling it up to temperatures higher than 1000°C the degree of intergranular micro-cracking became significant.

On the other hand, the 12 μm grain size material showed straight from the beginning a very low thermal expansion when cycled up to 500, 700, 900 and 1100°C. The average coefficient of thermal expansion between 20 and 1100°C was 1.1×10^{-6} K^{-1}. This indicates that the 12 μm grain size aluminium titanate had an extensive degree of intergranular microcracking.

The flexural strength and thermal shock resistance results are summarised in Fig. 1. The graphs show the original values of the so called Modulus of Rupture (MoR) in 4 point bending tests, as well as the MoR values obtained after water quenching aluminium titanate test bars from 600, 800, 1000, 1100 and 1200°C.

From the original values of the flexural strength one can deduce that the AT test bar sintered at 1300°C had probably no or very few microcracks. On the other hand, the test bar sintered at 1400°C had perhaps a reduced degree of microcracking, while the third bar sintered at 1450°C was probably in quite an advanced state of in-

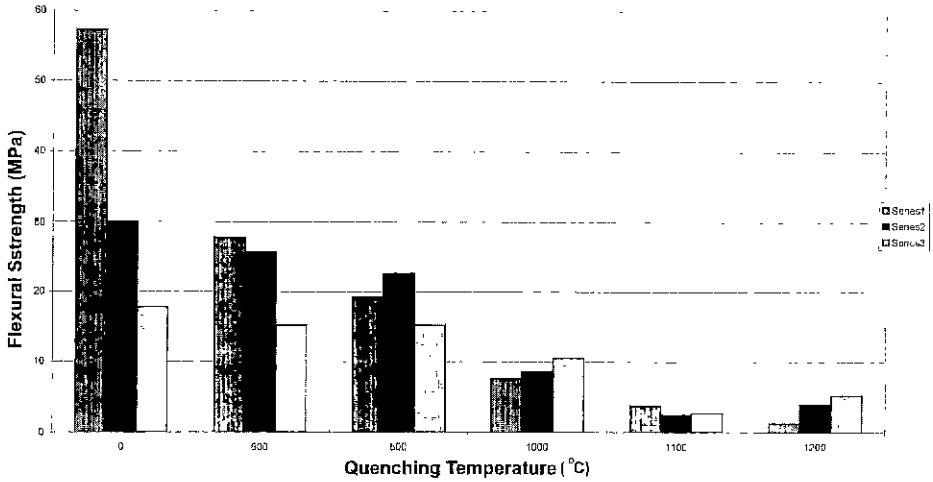

Fig. 1. Flexural strength vs. quenching temperature (Series 1: Sintered at 1300°C, Series 2· sintered at 1400°C, Series 3: sintered at 1450°C).

tergranular microcracking.

Taking into consideration the definition of the thermal shock resistance as the quenching temperature drop ΔT_c at which first a drastic decrease in strength occurs, it follows that the aluminium titanate sintered at 1300°C had a thermal shock resistance of no more than 600 K, while that sintered at 1400°C had an outstanding thermal shock resistance of 1000 K.

On the other hand, although the test bar sintered at 1450°C had a similarly high thermal shock resistance, its much to low mechanical strength could be a deterrent for many applications.

We deliberately left the results of the density and porosity measurements at the end of our discussion. We actually want to make the point that these properties can be used as a simple and efficient method of control of the intergranular microcracking for achieving optimal thermal shock resistance.

Variations of sintered bulk density, apparent solid density and apparent porosity vs. sintering temperature are presented in Fig. 2. For sintering temperatures increasing from 1300 to 1425°C there is an expected trend in the bulk density and apparent porosity values, while for 1450°C the trend is obviously reversed.

The variation of the apparent solid density suggests that with increasing sintering temperature an increasing number of individual, isolated microcracks, acting like closed (internal) porosity, is occurring. For sintering temperatures of 1450°C and higher the intergranular microcracks become probably generalised, interconnected to a certain extent, and act like open porosity this time.

It follows that a simple determination of density and porosity by the old method of Archimedes is able to bring very useful information and can accurately indicate the sintering conditions that would provide optimum thermal shock resistance.

In this case, for the particular raw materials and material composition we used, it follows that the best sintering temperature for thermal shock resistance would be 1400 to 1425°C. That would still ensure enough mechanical strength and, on the other hand would provide toughening through formation of discrete microcracks in a "reaction zone" ahead of an advancing crack, that would absorb energy and thus arrest the crack.

Sinter T (C)	1300	1350	1400	1425	1450
Db (g/c cm)	3.21	3.27	3.32	3.325	3.27
Das (g/c cm)	3.74	3.73	3.72	3.717	3.73
Pa (vol %)	14.20	12.15	10.77	10.640	12.29

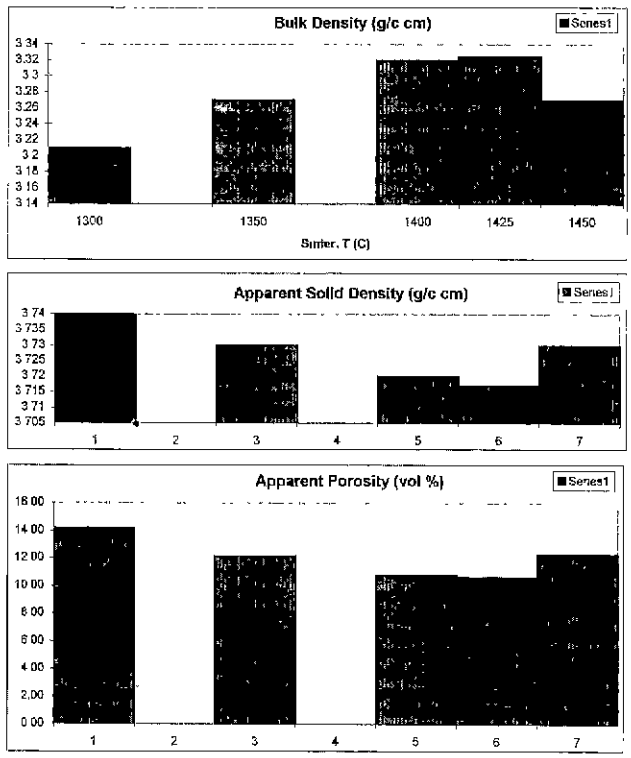

Fig. 2. Variationsof bulk density, apparent solid density and apparent porosity versus the sintering temperature.

IV. Conclusion

Density and porosity measurements can be used as a simple and reliable method of control of sintering processes aimed at optimising the microstructure of aluminium titanate ceramics for best thermal shock characteristics.

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