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Aluminium Titanate-Mullite 복합체 : Part2. 열충격성

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Aluminium Titanate-Mullite Composites : Part2. Thermal Shock Resistance

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초 록 여러 가지 화학 조성을 갖는 aluminium titanate-mullite 복합체는 Al_2O_3 분말을 알콜 분산 용액에서 $Si(OC_2H_5)_4$과 $Ti(OC_2H_5)_4$의 단계적인 가수 분해로 합성되었다. Mullite함량이 20-50vol%인 소결체(1600℃/2h)는 비교적 높은 강도와 낮은 열팽창 계수를 갖는 aluminium titanate을 개발할 수 있는 가능성을 보였다. 이와 같은 결과는 mullite로 인한 aluminium titanate의 입자 크기의 억제와 미세균열에 의하여 얻어졌다. aluminium titanate의 함량이 70-80vol% 복합재료는 우수한 열충격 저항성을 지녔으며 상온 강도는 31-45MPa이었다. 열충격 저항성, 영률, sound velocity와 열팽창 계수가 연구되었다.

Abstract Aluminium titanate-mullite composites with varying chemical compositions were prepared by the stepwise hydrolysis of $Si(OC_2H_5)_4$ and $Ti(OC_2H_5)_4$ in Al_2O_3 ethanolic colloidal dispersion. Sintered bodies having 20-50vol% mullite at 1600℃ for 2h have shown, that it is possible to develop an aluminium titanate with moderately high strength and low thermal expansion coefficient. This was obtained by inhibiting grain size of aluminium titanate with mullite and microcracks. Those with 80-70vol % aluminium titanate have excellent thermal shock resistance and has room-temperature strengths of 31-45MPa. The relation between thermal shock resistance and strength, Young's modulus, sound velocity and thermal expansion coefficient was discussed.

1. Introduction

Aluminium titanate (Al_2TiO_5) ceramics as structural material are known for their high refractoriness, very good corrosion resistance to molten metals, and excellent thermal shock resistance due to low thermal expansion, low Young's modulus, and low thermal conductivity [1]. The grain boundary microcracking occurs in aluminium titanate on cooling when the stress induced by the large expansion anisotropy of the three crystallographic directions exceeds the intrinsic strength of the material [2] and its tendency to decompose into Al_2O_3 and TiO_2 at temperature below 1300℃ limit, however, the application of Aluminium titanate [3].

Aluminium titanate components in engines are normally surrounded with liquid aluminium or cast iron, whereby the material combination of ceramic and metal requires a very good constructive adaptation of the two elements. During the solidification of the metal melt very high stresses are acting on the ceramic because of the clearly higher thermal expansion of metals. In order to avoid damages on the parts while they are surrounded with metals a

certain elasticity is necessary. The elasticity is only made possible by means of the given fine crack system. There, the cracks act as a stress absorber in which open crack flanks are closed during the solidification of the molten metal [4].

The compositions containing 10, 20, 30, and 50 vol% mullite were selected for examination, because the purpose of the present investigations was to moderate strength, microcracking structure and stabilized aluminium titanate by the limitation of β-Al_2TiO_5 grain with mullit content in order to obtain highly thermal-shock-resistant.

2. Experimental procedure

Tetraethylorthosilicate $Si(OC_2H_5)_4$ (Huels AG), Ethyltitanate $Ti(OC_2H_5)_4$ (Huels AG), α-Al_2O_3(A-16 SG;mean particle diameter : 0.3-0.5 ㎛ : Alcoa Chem) and Ethanol(Merck) were used as starting materials. Al_2TiO_5 and aluminium titanate-mullite composites were prepared by stepwise alkoxide hydrolysis of a molar ratio [$H_2O/Si(OC_2H_5)_4$] of 80 and [$H_2O/Ti(OC_2H_5)_4$] of 4 in α-Al_2O_3 powder ethanolic solutions(0.3-0.5㎛). Typical final solution concentrations were 0.4mol $Si(OC_2H_5)_4$, 0.3mol $Ti(OC_2H_5)_4$, 1.91mol NH_3 and 33.2 mol H_2O. The solution of coated powder was next centrifugated to remove the alcoholic solution, then washed with deionized water and redispersed in aquous NH_4OH solution(pH=10). Powder compacts were prepared by centrifugal casting followed by drying at room temperature for one day.

The thermal shock resistance of the subject materials was determined according to a water quenching process by way of analogy to a German industial standard [5]. Three specimens per material were heated to 950℃ for 15 min in a muffle furnance and quenched with flowing water to 20℃ for 15min. After drying at 110℃ for 30min, all specimens that withstood the thermal shock without spontaneously developing major cracks were subjected to the following tests in the cold condition :

The residual flexural strength of specimens ($7*7*70mm^3$) at room temperature water quenched from 950℃ temperature was measured by a universal-type testing machine. The span length was 40mm and the cross head speed was 0.2mm/min. The Young's modulus was measured by the resonance frequency method as a function of the number of quenching cycles, using bending specimens. The microstructural degradation of the cylinderical samples(Φ=25mm, h=35mm) was measured also by sound velocity with help of firm C. N. S. instrument LTD, "Pundit" apparatus. The thermal expansion coefficient(RT-1200℃) was determined on specimen($5*5*25mm^3$) using a dilatometer, heating rate 5℃/min and cooling rate 10℃/min in air, respectively.

3. Results and Discussion

Sintered unstabilized ATM1 exhibits a large grain growth of β-Al_2TiO_5 grain sizes between about 10-70㎛ with a small amount of dispersed corundum and rutile. The stabilized specimens ATM2 and ATM3 appear to have a smaller mean grain size of β-Al_2TiO_5(5-20㎛). Some of the large grains contained closed pores created during heating procedure. The mean grain diameter of ATM5 was 8 ㎛. Such a distribution of interlinked fine-mullite particles at grain boundaries would prevent grain growth of β-Al_2TiO_5. In all cases the tialite grain decreased with increasing mullite content and are surrounded by microcracks as shown in Figure 1.

Table 1 summarizes the phase compositions and the physical properties of the materials (1600℃/2h). The density of ATM-materials increased with increasing mullite content up to 20 vol% and then decreased at still higher mullite contents due to the increased the degree of microcracking (see figure 1). The ATM2-, ATM3- and ATM5-composition reached a density level of between 88.0% and 93.3% of the theoretical density, consisting of mainly two crystalline phases : stabilized

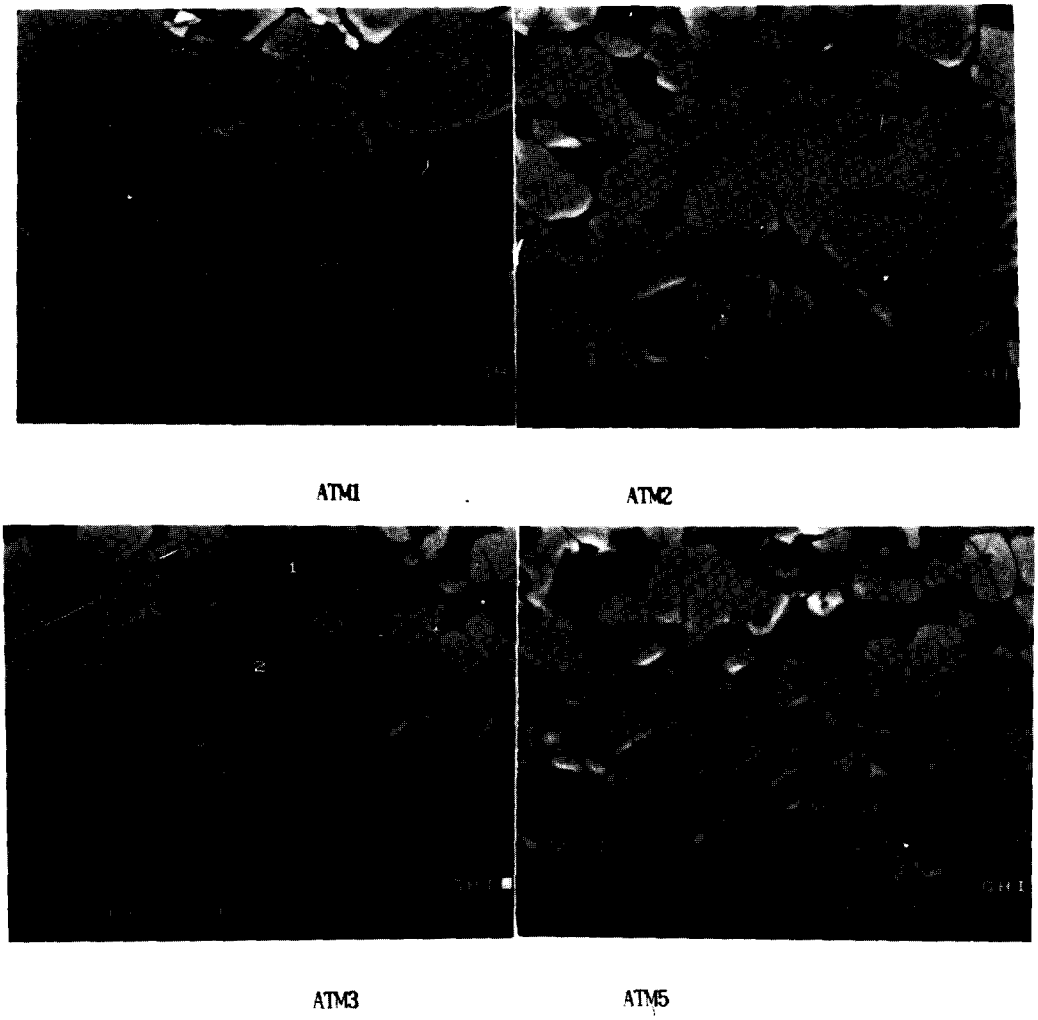

Fig. 1. Microstructure of sintered ATM-materials at 1600℃ for 2h(gray or 2 : AT, dim or 1 : mullite, bright : rutile, black : porosity)

Table. The phase compositions and the physical properties of the materials(1600℃/2h)

Materials	Mullite content	Phase composition	Bulk density	Relative density	Prosity	Average grain size of AT
	vol%		[g/cm³]	[%]	[%]	[㎛]
AT	0	AT+R+C	2.9	76.0	24	20
ATM1	10	AT+Mullite+L	3.3	88.2	11.8	40
ATM2	20	AT+Mullite	3.5	93.3	6.7	15
ATM3	30	AT+Mullite	3.3	88.0	12.0	14
ATM5	50	AT+Mullite	3.4	92.2	7.8	5

* Key : AT : β-Al_2TiO_5, R : Rutile, C : Corundum, L : Liquid phase

aluminium titanate and mullite. Above 10 vol % of mullite, The amount of liquid in composities were difficult to identify from this study due to the completely formation of multi-

phase composites, such as aluminium titanate-mullite. The grain size of β-Al_2TiO_5 in composites and the amount of porosity of ATM-materials decreased with increasing mullite content acounting for the observed increase in the relative density and thermal expansion coefficient (see Table 2).

Table 2 : Characteristics of specimens of aluminium titanate-mullite composites, after heat treatment at 1600℃ for 2h

Materials	Flexural strength σ_{bt} [N/mm²]	Young's modulus E [KN/mm²]	Thermal expansion coefficient α20℃-1200℃ 혹은 α(20℃-1200℃) [10 ⁻⁶K ⁻¹]	R_1 [K]	R_2 [W/m]
AT	20	13	0.68	1670	2505
ATM1	72	50	0.5	2189	3283
ATM2	31	11	0.9	2379	3568
ATM3	45	16	1.8	1187	1780
ATM5	47	17	2.0	1050	1575

Fig.2 shows the residual flexural strength of specimens having various composition after water quenching. Relatively high strength of 72 MPa was found in specimens having 90 vol % aluminium titanate, even though this material was still only 88.2% dense. This result can be attributed to the formation of grain boundary liquid phase during sintering. However, it gives sudden decrease of strehgth after one quenching cycle, but had moderate thermal shock resistance.

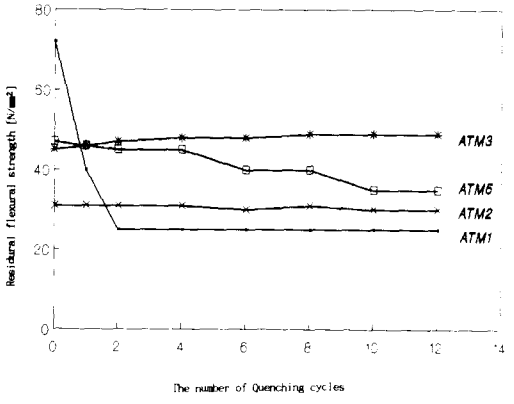

Fig. 2. Residural flexural strength of Al_2TiO_5-mullite composites with thermal shock in the water quench

The materials average strength having 80, 70, and 50 vol% aluminium titanate ranged from 31 to 47 MPa at room temperature and 30-47 MPa after 12 water quenching cycles. The strength values of ATM2 and ATM3 showed no distinct influence of tempering at 950℃ and it had excellent thermal shock resistance.

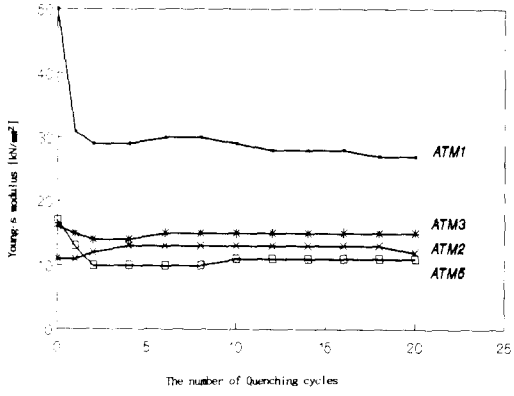

Fig. 3. Young's modulus of Al_2TiO_5-mullite composites with thermal shock in the water quench

As shown in figure 3, the Young's modulus was measured as a function of quenching number by the resonance method. One having 90 vol% aluminium titanate has higher Young's modulus of 50kN/mm² than the others, which whilst denser, contained appreciable amounts

of cracks on their grain boundaries. This Young's modulus of the ATM2-, ATM3- and ATM5-composites containing grain boundary microcracks would be caused by the constant in the area of contact across the sintered grain boundaries. Fig.4 shows the absolute sound velocity depend on the number of quenching. The decrease sound velocities of ATM1-composites is the degree of the degradation of microstructure. This depends on the microcracking and the density of microcracks. According to basic finding, higher microcrak densities also have positive effects on resistance to damage due to critical thermal shock [6]. The porosity dependence of the strengths and Young's moduli were best described [7] by Duckworth's exponential approach [8], where the open porosity has more effect on the modulus of elasticity than does the closed porosity(comparable to ATM1 and ATM2 or ATM3). ATM2-, ATM3 - and ATM5-composites show specially homogeneous microstructure with defined microcrack system(see Figure 1). This is grounds of the lower Young's modulus and with them lower flexural strength, but provided for simultaneously excellent thermal shock resistance.

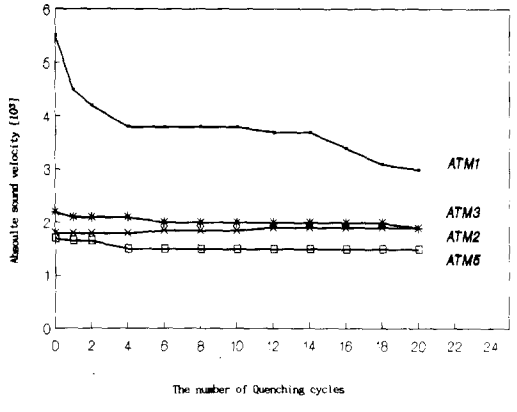

Fig. 4. Sound velocity of Al_2TiO_5-mullite composites with thermal shock in the water quench

Table 2 shown the effect of mullite contents on the Young's modulus, thermal expansion coefficient, flexural strength, and the thermal-stress-resistance factor(R_1, R_2).

The thermal expansion coefficient of studied materials was minimum at an Al_2TiO_5-content of 90 vol%(ATM1) and lies between 0.5-2.0 $*$ $10^{-6}K^{-1}$ in the temperature range RT-1200℃. SiO_2 additions of 3.44wt% did improve the strength of reaction-sintered material(ATM1) to 72 MPa with a low thermal expansion coefficient of 0.5-2.0 $*$ $10^{-6}K^{-1}$. This was attributed to the formation of a grain boundary liquid phase during sintering which aided densification and thus reduce microcracking, thereby increasing the strength. This result was presented in table 2 with the higher calculated value. In connection with thermal cycling behavior, differentiation can be made between resistance to crack formation and resistance to damage(crack propagation). The thermal shock resistance was theoretical calculated by the thermal stress parameters R_1 and R_2(pertaining to severe and mild quenching, respectively).

$$R_1 = \frac{\sigma_{bt}(1-\nu)}{\alpha E} \quad (1)$$

$$R_2 = R_1 * \lambda \quad (2)$$

Where R_1 and R_2 are a material constant that can be described as a material resistance factor for thermal stresses, σ_{bt} is the flexural strength, E is Young's modulus, α is the thermal expansion coefficient, ν is Poisson's ratio, and λ is the thermal conductivity, which is asumed to be constant(ν=0.24, λ=1.5 W/mK) in this study [9, 10]. Once the material's resistance to crack initiation has been exceeded, its resistance to damage(from crack propagation) becomes the decisive element of the thermal cycling behavior; it is described by the thermal stress parameter R_7 [111].

$$R_7 = \frac{\gamma_{wf} E}{\sigma_{bt}^2 (1-\nu)} \quad (3)$$

Where γ_{wf} is the specific fracture surface energy [12]. The above discussion of the dependence of σ_{bt}, E, ν on the mineral-phase content indicates that the resistance to damage (3) is not uniquely dependent in the same sense. The

fracture surface energy(not inverstigated here) was supposed to be determined primarily on the basis of microcracks, depending on the type and extent of the second phase, as indicated by the temperature dependence of stress -induced transformation and other result [13]. Due to σ^2_{br} the dominant influence of strength as a function of porosity affect the resistance to damage (3) more than (1) or (2). The specific fracture surface energy generally decreases exponentially with increasing porosity [14]. The last remaining materials("ATM2, ATM3, ATM5" in fig. 3, 4) suffered no measurable damage. Considering the material's 6.7-12.0 vol.% porosity and microcracks, these can be attributed to very high resistance to damage. This conclusion was reached from the low Young's modulus, low strength, and low thermal expansion coefficient($0.9-2.0 * 10^{-6}K^{-1}$) of the aluminium titanate-mullite composites caused by presence of microcracks.

4. Conclusion

Aluminium titanate was well stabilized by the limitation of grain size (5-15㎛) of β-Al_2TiO_5 with mullite(20-50vol%). Young's modulus and flexural strength were maxium at a mullite content 10 vol% but this materials is accompanied by a realized lower thermal shock resistance. The result can be attributed to fewer grain boundary microcracks as a stress absorber. With increasing mullite content more than 10vol%, Young's modulus, thermal expansion coefficient and room temperature strength increased. Those with 80, 70, and 50vol% aluminium titnate have excellent thermal shock resistance due to the presence of fine-grained microcracks.

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