自發韌化氧化鋯韌化莫來石之製備研究

Preparation of in-situ Reinforced Zirconia Toughened Mullite (ZTM)

計劃編號：NSC 89-2216-E-002-023

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一、摘要：

1.1 英文摘要：

The Zirconia-toughened mullite (ZTM) is prepared by reaction sintering of kaolin, zircon and alumina. The reaction between the starting materials results in mullite and zirconia, the aspect ratio of mullite is larger than unity. The comparison is made to the system of alumina and zircon. The presence of kaolin lowers the temperature to complete the reactions, and promotes the densification through the formation of a liquid phase during sintering.

Keywords: in-situ reinforced, mullite, microstructural design, mechanical properties, kaolinite, alumina, processing.

1.2 中文摘要：

本研究探討以高嶺土、鋯英砂及氧化鋁為原料，探討反應燒結方式製備氧化鋯韌化莫來石的製程，反應燒結後所得的莫來石晶粒長寬比大於 1，當與氧化鋁-鋯英砂反應燒結系統比較時，高嶺土的添加可產生液相並降低燒結溫度。

關鍵字：自發韌化、莫來石、微結構設計、高嶺土、氧化鋯韌化莫來石。

二、計劃緣由與目的：

In the last ten years, there are many breakthroughs as far as the development of ceramic-matrix composites is concerned. One of the breakthroughs is the exploration of the in-situ reacted microstructure. The mechanical properties of the silicon nitride are thus enhanced significantly through this development. Date back to four years ago, we have found that the microstructure of mullite prepared by using kaolin is very similar to that of the in-situ reacted silicon nitride. We have thus carried out the works on in-situ reacted systems, such as in-situ reacted mullite, since then. Part of the results were published recently [1,2]. In the present study, the processing of the preparation of in-situ reacted zirconia toughened mullite is investigated.

The objective of the present study is to develop a ceramic-matrix composite with high economic potential. There are three features for this study:

a. Kaolinite, alumina and zircon are used as the starting materials. The reaction sintering technique are used to prepare the in-situ reacted zirconia toughened mullite. Since the raw materials are readily available, the cost of the developed composites is expected to be low. The economic potential of the composite is therefore high.

b. Both in-situ reacted mullite and zirconia are existed within the composites, the mechanical properties of the mullite can thus be improved due to the presence of zirconia.

c. There is little systematic study on the interactions between the in-situ reinforced microstructure and the transformation toughening yet.

三、研究方法

The raw materials used in the present study are kaolin (AKIMA 35, Akima Co., Malaysia), alumina (AES-11, Sumitomo Chem., Japan, 99.8% Al_2O_3) and zircon (Australia) powders. The mixing was carried out in ethyl alcohol with a turbo-mixer. The composition of the kaolin and zircon powders was determined with the induced coupled plasma emission spectroscopy (ICP). The grinding media was zirconia balls and milling time was 4 hours. After drying, the dried lumps were crushed and passed through a #100 plastic sieve. The powder compacts were prepared by the die-pressing technique. The pressure applied was 27 MPa. The firing was carried out at a temperature varied from 1400℃ to 1600℃ for 1 hour. The heating rate and cooling rate were 5 ℃/min. The phase identification was performed by X-ray diffractometry. The final density was determined by Archimedes' method. The microstructure was observed by scanning electron microscopy (SEM). To reveal the morphology of mullite grains, a concentrated hydrofluoric acid was used as etching solution.

四、結果與討論：

The compositions of kaolin and zircon as determined by ICP are shown in Table 1. The five systems investigated in the present study are (1) kaolin, (2) kaolin + alumina, (3) zircon + alumina, (4) zircon + kaolin and (5) kaolin + alumina + zircon. The density of the five systems after firing at 1400C, 1500C and 1600C for 1 hour is shown in Table 2. The XRD patterns of the fired specimens are shown in Fig. 1. The microstructures of the 5 systems after sintering at 1600℃ for 1 hour are shown in Fig. 2.

The only crystalline phase after firing kaolin at 1600℃ is mullite. There is some excess silica in the form of quartz and some impurities in the starting material, see Table 1, apart from mullite, a glassy phase is thus also formed in the sintered specimen.

The reaction as following was taken place during the sintering of the powder mixtures of kaolinite and alumina,

$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O + 2Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2H_2O$ (1). Therefore, the phase presented in the fired (kaolin + alumina) specimen is mullite. Furthermore, alumina can interact with the excess silica in kaolin, the amount of glassy phase is reduced comparing to that of the pure kaolin specimen.

Alumina and zircon can react with each other to form mullite and zirconia as

$3Al_2O_3 + 2ZrSiO_4 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2ZrO_2$.......(2)

After firing at 1600C for 1 hour, residual alumina can still be detected. The reaction between alumina and zircon is thus a kinetically slow one.

Zircon is a stable phase in the presence of kaolin. Kaolin transforms to mullite as the case for pure kaolin. However, the presence of zircon enhanced the grain growth of mullite grains, Fig. 2(d). It may due to the presence of zircon increase the amount of glass phase.

Residual alumina can hardly be found in the (kaolin + alumina + zircon) specimen after firing at 1600℃ for 1 hour. Furthermore, zircon is fully transformed to monoclinic zirconia after firing. It indicates that the addition of kaolin promotes the decomposition of zircon; furthermore, the reaction between zircon and alumina is enhanced.

五、結論：

In the present study, the interactions between kaolin, alumina and zircon are investigated. The resulting microstructure of the systems after reaction sintering systems are observed. Zirconia toughened mullite can be prepared by using kaolin, alumina and zircon a starting material. The presence of kaolin promoted the reactions between alumina and zircon.

六、參考文獻：

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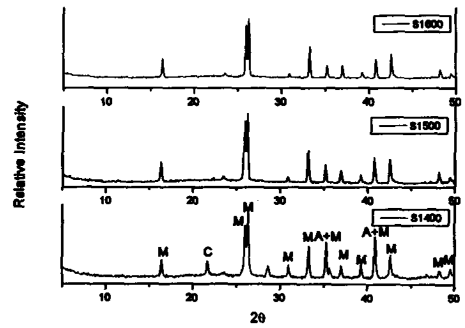
Table 1. The compositions of kaolin and zircon. (in wt%)

Composition	Kaolin	Zircon
Al_2O_3	35.730	0.670
BaO	0.050	0.040
CaO	0.050	0.060
Fe_2O_3	0.858	0.088
K_2O	1.180	***
MgO	0.220	0.220
Na_2O	***	***
SiO_2	48.600	33.800
TiO_2	0.440	0.228
ZrO_2	***	64.400
ZnO	***	***
Ig. Loss	12.615	0.110

Table 2. The absolute density of specimens investigated in the present study.

Density (g/cm^3)	1400℃	1500℃	1600℃
Kaolin + Alumina	2.656	2.616	2.879
Zircon + Alumina	3.341	3.542	3.486
Zircon + Kaolin	3.008	3.043	2.550
Kaolin + Alumina +Zircon	2.672	2.631	3.938



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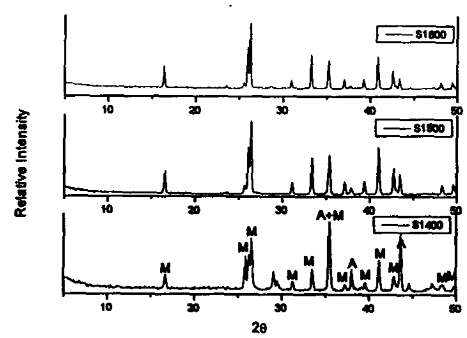

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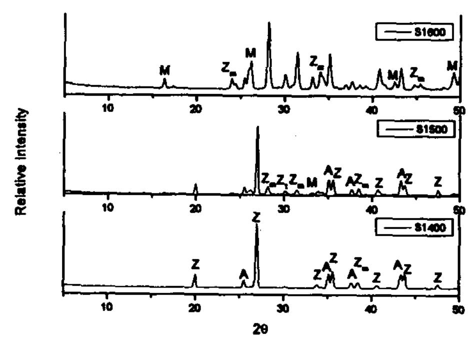

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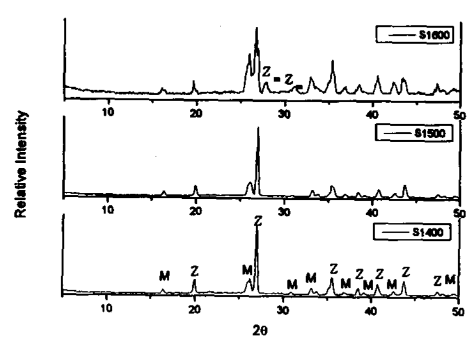

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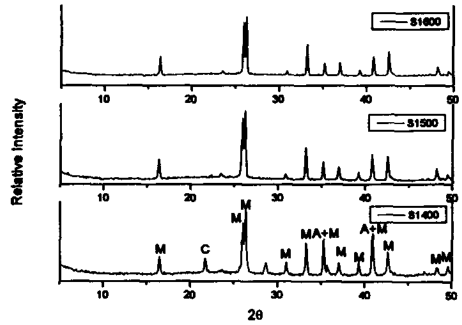

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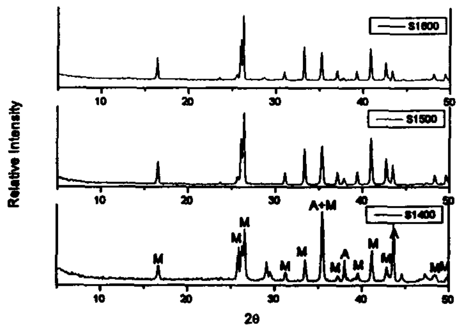

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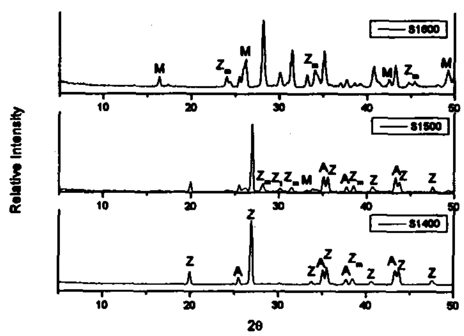

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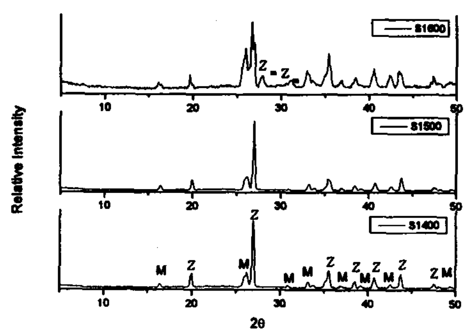

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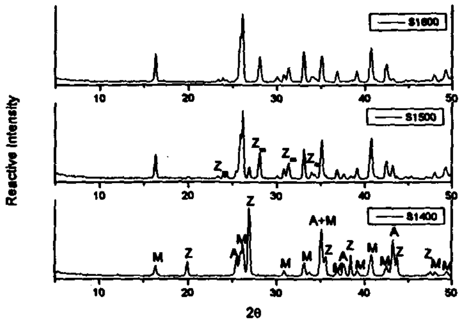

(e)

Fig.1 The XRD patterns of (a) Kaolin, (b) Kaolin+Alumina, (c) Alumina+Zircon, (d) Zircon+Kaolin, (e) Kaolin+Alumina+Zircon specimens after firing at 1400℃, 1500℃ and 1600 ℃ for 1hour.

(a)

(b)

(c)

(d)

(e)

Fig.2 The fracture surface of (a) Kaolin, (b) Kaolin+Alumina, (c) Alumina+Zircon, (d)Zircon+Kaolin, (e)Kaolin+Alumina+Zircon specimens after firing at 1600℃ for 1 hour.