

# **A fabrication on continuous coal ash derived ceramic fiber**

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## **ABSTRACT**

The objective for the high valued utilization on coal ash in Taiwan textile research institute(TTRI), based on the concerned issues of energy conservation, environment protection and sustainable development, has focused on the development of the coal ash derived ceramic fibers with heat resisted, heat insulated and strong mechanical properties utilizing the reaction byproduct from the thermal power generation. The synthesis of coal ash derived spinnable precursors was started with a core technique, and the following fabrication of coal ash derived ceramic fibers was prepared with a suitable spinning process and high temperature treatment. The results indicate that the key for the spinnable characteristics of coal ash derived spinnable precursors is affected by the solid content and phase composition of coal ash. On the other hands, the morphology, microstructure and ultimate phase composition of coal ash derived ceramic fibers were dominated by high temperature treatment. The current research status on TTRI is that the average diameter of coal ash derived ceramic fibers is 10 $\mu$ m to 30 $\mu$ m. A continuous spinnable length of the fibers could be achieved to 10 meters, and the major phase composition of that are mullite and alumina phase.

## Introduction

Ceramic fibers are considered as an important fibrous material with a heat resisted, heat insulated and strong mechanical properties. With these superior properties, ceramic fibers and their fabric products are often applied to the applications of space, heat insulation for energy conservation or anti-corrosion at high temperature [1]. The common raw materials for the synthesis of ceramic fibers come from the alumina, silica and their mixture. Mullite could be considered as the mixture of the alumina and silica in specific proportion of alumina/silica (72/28), which is proposed to be more able to utilize at high working temperature [2-4]. Some additives of zirconia and magnesia are often used as an inhibitor for the growth of crack and could be strengthen the mechanical properties effectively [5-9]. In addition to the alumina fibers, silica fibers and mullite fibers, several different fibrous materials like amorphous alkaline earth silicate and basalt from minerals or fused silica and silicon carbide from artificial are also mentioned as the potential materials for high temperature application but limited by their cost and stability during the process. Two common synthetic processes of melt-spinning and sol-gel spinning are common processes for the fabrication of ceramic fibers. Usually, the thermal mechanical properties of ceramic fiber prepared by a melt-spinning process is relative lower than the one fabricated by a sol-gel spinning method. In a practical point of view, sol-gel method with several advantages such as lower synthetic temperature during the synthetic process, higher purity for precursor, and better spinnability for the fabrication of gel fiber is often applied to the production in a commercial scale [3,4,9-12]. Two commercial products of Nextel® products from 3M Company and Altex® products from Sumimoto Company are utilized the sol-gel method. But with a limitation on the cost of the production, stability during the synthesis and the grain growth resulted by the high temperature treatment, a suitable recipe for sol-gel process and an optimized spinning process are still under developing.

Coal ash, a by-product of coal combustion in thermal power generation, could be considered as a complex mixture of ceramic phases. The major application for coal ash is for the concrete application, other applications are including road base construction, soil amendment, zeolite synthesis, and using as a filler in polymers [13,14]. Silica and alumina are two major component of coal ash and are suitable as the additives for modification of phase composition. In this study, a simple approach for coal ash derived ceramic fiber started from the synthesis of coal ash derived spinnable precursors using the sol-gel method. The

grounded coal ash nanoparticles with an average size distribution were used as additives in the alumina gel system. The following fabrication of coal ash derived ceramic fibers was prepared with a suitable spinning process and high temperature treatment. The morphology, microstructure and phase composition were characterized by the SEM and XRD. The experimental results indicated that the average diameter of coal ash derived ceramic fibers is 10 $\mu$ m to 30 $\mu$ m. A continuous spinnable length of the fibers could be achieved to 10 meters, and the major phase composition of that are mullite and alumina phase.

## **Experimental**

The coal ash derived ceramic fibers were prepared with a dry spinning process and high temperature treatment using a coal ash nanoparticles contained alumina gel as the spinning precursor. The coal ash nanoparticles with an average size distribution were first grounded using ball mill process. After a continuous grinding of 24 hours, a surface modification to the coal ash nanoparticles was carried out by a silanized functionalization in an ethanol solution at 338K for 1hour. On the other hand, the alumina gel was synthesized by a sol-gel method using a pre-polymerization route, as shown in figure 1. Aluminum nitrite (AN) and aluminum isopropoxide (AIP) were selected as the aluminum source for the formation of aluminum gel. A mixture of AN/AIP with a specific ratio was dissolved in an aqueous solution with approximately pH value of 2 adjusting by the lactic acid. After a suitable condensation process, the silanized coal ash nanoparticles were soon added into alumina gel with different contents using a polyvinyl alcohol (PVA) as spinning add. The coal ash nanoparticles contained alumina gel fiber could be obtained by a dry spinning process and following drying process under a controlled humidity environment. The dried gel fibers were then heat treated at temperatures of 1273k to 1573k. The cross-section morphology of coal ash derived ceramic fiber was observed field emission scanning electron microscopy (FESEM), and the element analysis of coal ash particles was investigated by an energy-dispersive X-ray spectroscopy (EDX). The microstructure and their crystallinity of the coal ash derived ceramic fiber were characterized by X-ray diffraction method. The amounts of phase composition on coal ash nanoparticles were measured by an X-ray Fluorescence spectrometer (XRF).

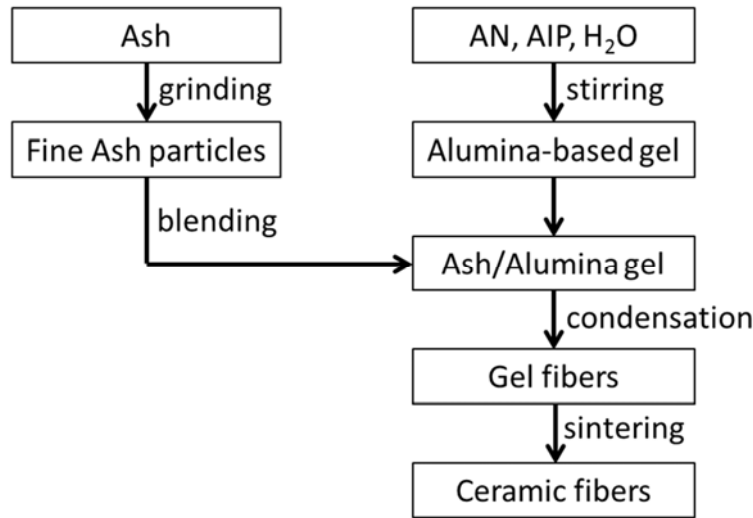


Figure 1 the flow chart for the fabrication of coal ash derived ceramic fibers.

## Results and Discussion

Figure 2 shows the SEM observation and element analysis results of as-received coal ash powders at different location by an energy-dispersive X-ray spectroscopy. As shown in figure 2, a spherical morphology for the majority of as-received coal ash powders was observed and also an obvious aggregation of coal ash powders was observed. The average particle distribution of as-received coal ash powders is around  $1\mu\text{m}$ - $100\mu\text{m}$ . In the results of element analysis, the major elements of as-received coal ash powders are silicone and aluminum at each location. In addition, a moderate quantity of iron and a small amount of alkali metal and alkaline-earth metal are also detected, but their distribution was not uniform at each location. To confirm the accurate phase composition of as-received coal ash powders, XRF analysis was performed on as-received coal ash powders and the results are presented in table 1. As shown in table 1, the total amount of mixture of silica and alumina was over 75%, and the amount of silica is almost two times to that of alumina. Obvious amounts of calcium oxide and ferric oxide were also detected. It is suggested that the element analytic results indicated an inhomogeneous distribution of metal oxide and alkali metal oxide on as-received coal ash powders. In addition, a lower dispersivity of spinning precursor usually comes from an excessively large particle size distribution of additive fillers and further causes the instability during fiber spinning process. In other words, a uniformed particle size distribution for the fillers in the spinning precursors is the one of the key to control the stability during fiber spinning and also affect the final phase

composition of ceramic fiber after the high temperature treatment.

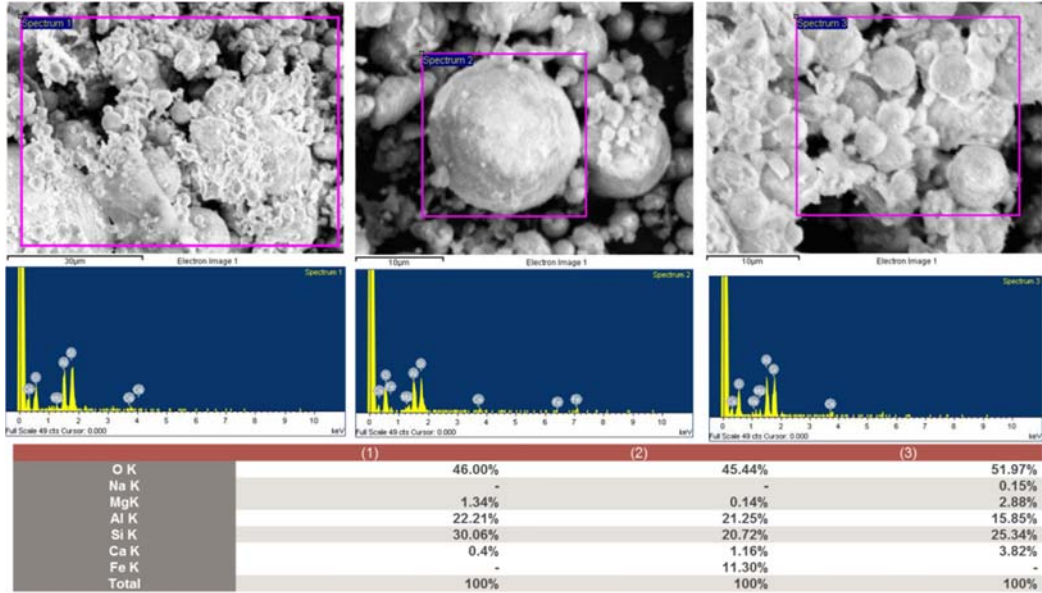


Figure 2 SEM images of as-received coal ash powders at different location and their EDX analysis.

Table 1 phase composition of as-received coal ash powders

Composition	Sum	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO
Ratio(%)	100.00	49.57	25.54	9.49	6.31	2.03	1.60

Figure 3 shows the morphology of coal ash nanoparticles after grounded for 24 hours. A quite uniform particle size distribution of coal ash nanoparticles could be obtained. The average size for coal ash nanoparticles was around 0.5µm-1µm. A slightly aggregation induced by the electrostatic force for the nanoparticles were also observed. It is suggested that a suitable surface modification for coal ash nanoparticles was also required.

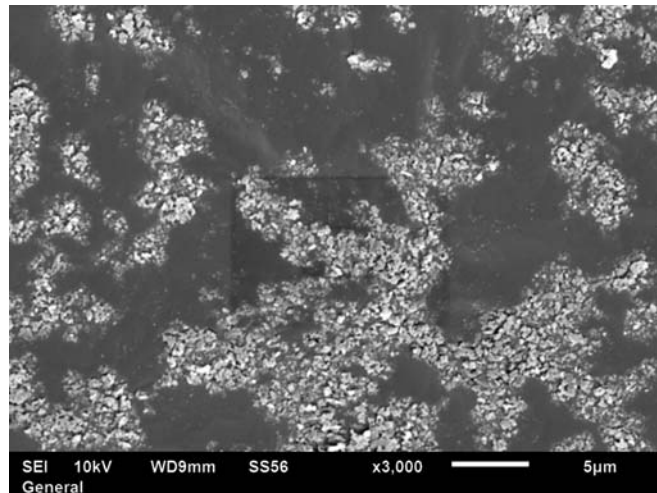


Figure 3 SEM morphology of coal ash nanoparticles after grounded for 24 hours.

Figure 4 shows the cross-sectional morphology of coal ash derived ceramic fibers under a heat treatment temperature of 1300 °C and the possible mechanism for the coal ash nanoparticles dispersed in alumina fiber. As indicated in figure 4(b), a uniform dispersion of coal ash nanoparticles with a range of 0.5µm-1µm was found in alumina fiber. No obvious agglomeration of coal ash nanoparticles or internal cracks could be observed in the cross-section of alumina gel fiber. It is suggested that a uniform dispersed coal ash particles in alumina fiber leads to a restraint of the crack growth and further improve the mechanical and thermal properties of coal ash derived ceramic fibers.

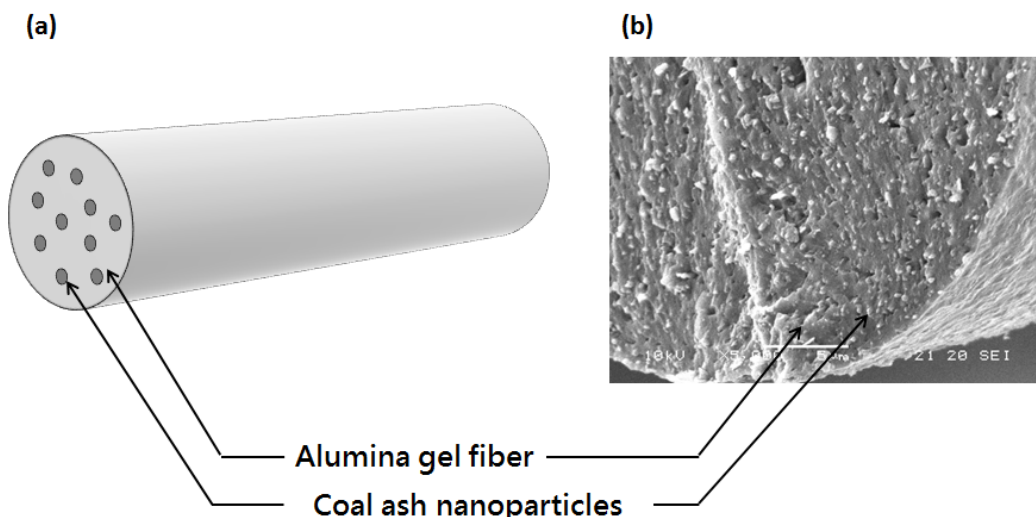


Figure 4 the cross-sectional morphology of coal ash derived ceramic fibers under a heat treatment temperature of 1300°C and their schematic diagrams.

Figure 5 shows the morphologies of coal ash derived ceramic fiber and alumina fiber after a high temperature treatment with two different temperature of 1000

°C and 1300°C. As shown in figure 5(a), an obvious apophysis on the surface of the coal ash derived fibers could be observed after a 1000°C heat treatment. In addition, no obvious cracks or vacancies were found on their surface. On the observation of 1000°C heat treated ceramic fiber in a cross section view (figure 5(b)), the as-dispersed coal ash nanoparticles inside the gel fiber has no longer been observed, and also no significant internal cracks could be observed inside the fiber. When increasing the heat treatment temperature to 1300°C, a notable granular apophysis could be found on the surface of coal ash derived fibers, and only few small vacancies on the fiber surface could be observed, as shown in figure 5(c). Figure 5 (d) shows that no significant internal cracks or vacancies could be observed inside the 1300°C heat treated ceramic fibers. In addition, no obvious grain boundaries inside the fibers means a strong restraint effect to the grain growth induced by high temperature would remain the average grain sizes of alumina fibers and further contains their mechanical properties at higher temperature. For the comparison to the alumina fiber treated at 1300°C, regardless the location of the alumina fibers, an obvious cracks and grain growth could be observed inside or outside the fibers. It is suggested that a well dispersed coal ash nanoparticles play an important role as an inhibitor for the grain growth due to the temperature effect and also as one for the growth of internal cracks.

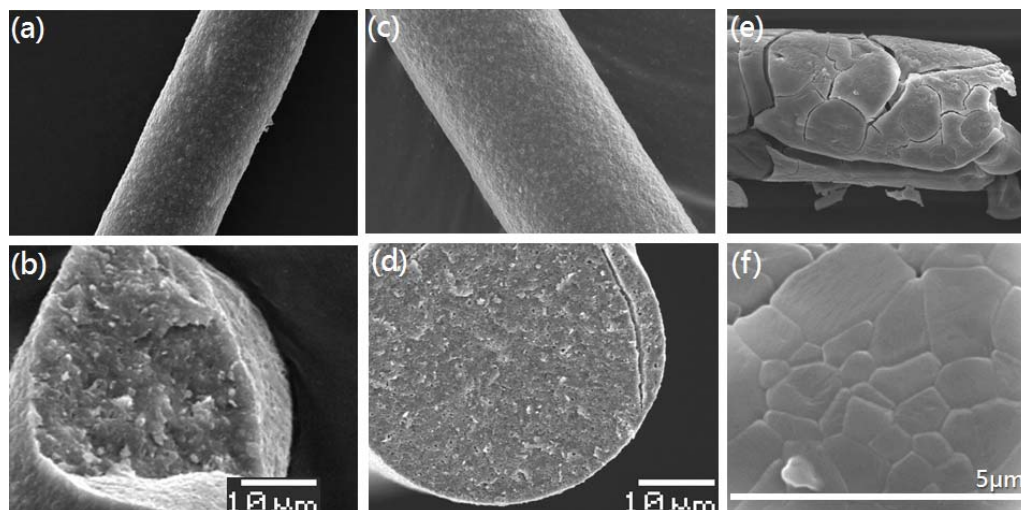


Figure 5 SEM morphologies of coal ash derived ceramic fiber and alumina fiber after a high temperature treatment with two different temperature of 1000°C and 1300°C.

The other function from added coal ash nanoparticles was their complex phase compositions. As mentioned before, the major phase compositions are silica

and alumina and the total amounts of silica is around 50%. Since the silica could be considered as a source of silicone, a well dispersed coal ash nanoparticles would not only provide a function of inhibitor for grain growth but also as an initiator for phase transition from a alumina phase to a mullite phase. In addition, the remained alkaline earth oxide and alkali metal oxide in coal ash nanoparticles usually are considered as a sintering aid for the enhancement surface diffusion on the interface between nanoparticles to the fibers matrix by decreasing the melting temperature. In our study, the presence of calcium oxide and magnesia would promote the decrease of the melting temperature and further caused interface sintering by a relative lower meting temperature. Figure 6 shows the XRD pattern of phase composition of alumina ceramic fiber and coal ash derived ceramic fiber at heat treated temperature of 1000°C and 1300°C. As shown in figure 6, only amorphous phase could be observed for both of alumina ceramic fiber and coal ash derived ceramic fiber when heat treated at 1000°C. Since increasing the heat temperature to 1300°C, a single phase of alumina with higher crystallinity could be observed at alumina ceramic fiber, and the average particle size of 49 nm were calculated using the bragg's law. On the contrary to the alumina ceramic fiber, much more complex phase compositions could be detected due to the added coal ash nanoparticles. As show in figure 6, not only the alumina phase could be observed in coal ash derived ceramic fiber, but also a mullite phase could be clearly found at such lower temperature. In addition, a much lower crystallinity of 36 nm for alumina phase suggested that the presence of coal ash nanoparticles would enhance the phase transition at lower temperature by those remained component.



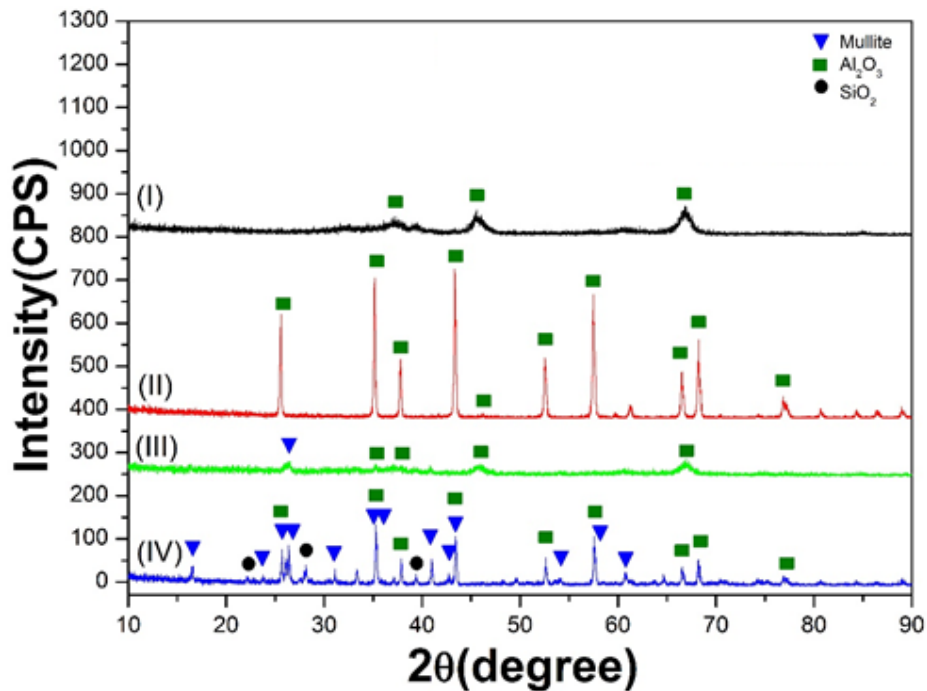


Figure 6 XRD pattern of phase composition of alumina ceramic fiber and coal ash derived ceramic fiber at heat treated temperature of 1000°C and 1300°C.

## Conclusion

In summary, a simple approach for coal ash derived ceramic fiber starting from a synthesis of spinnable precursor using the sol-gel method was reported. The following fabrication of coal ash derived ceramic fibers was prepared with a suitable spinning process and high temperature treatment. The experimental results indicate that the key for the spinnable characteristics of coal ash derived spinnable precursors is affected by the solid content and phase composition of coal ash. On the other hand, the morphology, microstructure and ultimate phase composition of coal ash derived ceramic fibers were dominated by high temperature treatment. The SEM images show that a well dispersed coal ash nanoparticles in gel fiber matrix could be obtained after a suitable grinding process and silanized functionalization. The SEM and XRD results both demonstrated that the coal ash nanoparticles play an important role not only as an inhibitor for grain growth but also as an initiator for phase transition from an alumina phase to a mullite phase at lower heat treated temperature. The current research status on TTRI is that the average diameter of coal ash derived ceramic fibers is 10µm to 30µm. A continuous spinnable length of the fibers could be achieved to 10 meters, and the major phase composition of that are

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## Reference

- [1] Schawaller, D., Clauß, B., and Buchmeiser, MR. *Macromol. Mater. Eng.* 2012, 297, P. 502.
- [2] Tan, H. *Journal of Ceramic Processing Research.* 2012, 13(5), p. 575.
- [3] Chen, X., Gu, L. *Journal of Non-Crystalline Solids* 2009, 355, p. 2415.
- [4] Chen, X., Gu, L. *Materials Research Bulletin* 2009, 44, P.865.
- [5] Kurokawa, Y., Utsumi, K., Takamizama, H. *J. Am. Ceram. Soc.* Vol. 1988, 71, p.588.
- [6] Kuramoto, N., Taniguchi, H. *J.Mater. Sci. Lett.* 1984, 3, p. 471.
- [7] Souto, P.M., Menezes, R.R., Kiminami, R.H.G.A. *Journal of materials processing technology* 2009, 209, p.548.
- [8] Ouali, A., Heraiz, M., Sahnoune, F., Belhouchet, H., Fatmi, M., Saheb, N. *American Journal of Modern Physics* 2013, 2(5), p. 270.
- [9] Wang, W., Weng, D., Wu, XD. *Progress in Natural Science: Materials International* 2011, 21, p. 117.
- [10] Chandradass, J., Balasubramanian, M. *Journal of Materials Processing Technology* 2006, 173, p. 275.
- [11] Tan, H.B., Ma, X.L., Fu, MX. *Bull. Mater. Sci.*, 2013, 36(1), p. 153.
- [12] Venkatesh, R., Roy Ramanan, S. *Journal of the European Ceramic Society* 2000, 20, p. 2543.
- [13] Chandradass, J., Balasubramanian, M. *Fuel* 2012, 97, p. 1.
- [14] Yao, Z.T., Ji, X.S., Sarker, P.K., Tang J.H., Ge, L.Q., Xi, M.S., Xi, Y.Q. *Earth-Science Reviews* 2015, 141, p. 105.