A Study of Cordierite Ceramics Synthesis From Serpentine Tailing and Kaolin Tailing

P. Zhu1, L.Y. Wang1, D. Hong1, M. Zhou2

1 College of environmental and chemical Engineering, Shanghai University, 99 Shangda Road, Shanghai 200444, People’s Republic of China.

2 Semiconductor Manufacturing International (Shanghai) Corporation, 18 Zhangjiang Road, Shanghai 201203, People’s Republic of China.

Abstract:
Cordierite ceramics was synthesized using a composition prepared by the mixture of three different materials: waste serpentine mine tailing (WST), waste kaolin mine tailing (WKT) and alumina. The formation of cordierite was achieved with the solid-state sintering reactions at 1350 °C for 3 h. The synthesized cordierite ceramics was characterized by X-ray diffractometer (XRD), thermal analysis (TG-DTA), and SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectrometer). The XRD analysis results showed the cordierite with typical rhombic system as a major phase, and its compositions consisted of O, Al, Si and Mg by means of SEM-EDS.

Keywords: Serpentine mine tailing, Kaolin mine tailing, Cordierite ceramics, Sintering, Solid phase reaction.

1. Introduction

Natural cordierite having a chemical composition of (Mg,Fe)2Al4Si5O18 is a magnesium aluminosilicate mineral, occurring very rare in nature. Cordierite ceramics have low thermal expansion coefficient, excellent thermal shock resistance, low dielectric constant, high volume resistivity, high chemical durability, high refractoriness and high mechanical strength. Therefore, they are widely used as honeycomb-shaped catalyst carriers in automobile exhaust systems, as substrate material for integrated circuit boards, as thermal shock-resistant tableware, as heat exchange for gas turbines, as porous ceramics and as refractory materials [1-8].

Several methods have been proposed to synthesize cordierite over decades including: 1) solid-state reaction of MgO, Al2O3 and SiO2 or their precursors [9, 10] and 2) wet chemical methods such as sol–gel processes, hydrolysis, spraypyrolysis, and combustion synthesis [11-15]. The disadvantages of these processes include expensive starting materials, low yields and complicated processing procedures, which are not suitable for large-scale low-cost applications. From the viewpoint of saving cost, some of the starting mineral raw materials reported in literature include talc, sepiolite, kaolin, silica, gibbsite, and kaolinitic clay [16-20].

As a low cost alternative method, reaction sintering is proposed using inexpensive materials such as kaolin and talc, andalusite, industrial wastes and Al-rich anodising sludge [7, 21-24]. This method is quite suitable to directly prepare cordierite ceramics during a one-
step sintering process, in accordance with the concept of sustainable development. However, there are few reports on preparation of cordierite ceramics using serpentine (or serpentine tailing) as starting materials. Serpentine, Mg$_2$Si$_2$O$_5$(OH)$_4$, is a kind of hydrated magnesium silicate. The major applications for serpentine are dimension stone and flux materials. The serpentine rock is crushed to produce many waste serpentine tailing (WKT), and it is estimated that a total of no less than a thousand million tons of WST was produced from Yiyang county, Jiangxi province, China. WST compositions of SiO$_2$ (34.3%), MgO (44.1%), and Fe$_2$O$_3$ (6%) is rich SiO$_2$ and MgO so that cordierite ceramics can be produced if a suitable amount of alumina source is added based on the MgO-Al$_2$O$_3$-SiO$_2$ ternary phase diagram [25-28].

The main purpose of the present study was to produce cordierite ceramics. WST, waste kaolin tailing (WKT) and alumina are selected as the starting materials to achieve this purpose. This could be another way for potential application of WST and WKT in China.

2. Experimental

The starting raw materials used in this study were WST, WKT, and alumina from China. WST that was produced from the serpentine rocks crushed for flux material and building decoration had a chemical compositions of SiO$_2$ (34.3%), MgO (37.5%), Fe$_2$O$_3$ (6%), Al$_2$O$_3$ (0.2%) and CaO (0.45%). WKT was produced from mining kaolin for porcelain raw materials, and its chemical compositions contained SiO$_2$ (66.7%), Al$_2$O$_3$ (15%), MgO (0.4%), CaO (0.2%) and Fe$_2$O$_3$ (0.2%).

Based on the composition of WST and WKT and the MgO-Al$_2$O$_3$-SiO$_2$ phase diagram, WST, WKT, and alumina with the content of 30%, 50% and 20% in the region of cordierite formation) were ground into sizes below 100µm, and they were sufficiently fine to be mixed homogeneously. The mixture was mixed with the organic binder (Glycerol reagent /raw materials: 8%), which was pressed into cylindrical pellets (13 mm diameter and 3 mm height). The samples were placed in a room of 25 °C for two days, and were dried at 105 °C, finally, were roasted in the high-temperature resistance furnace. The heating of sample started at 25 °C, and then the sample was sintered in air up to 1000, 1200, and 1350 °C at the ramping rate is 5 °C min$^{-1}$. Finally, the sample was naturally cooled until they reached the room temperature.

The mixture of WST, WKT and alumina weighed from 4 to 10 mg in mass, and they were put into a Pt-Rh crucible, which was analyzed between 25 °C and 1000 °C at a heating rate of 5 °C min$^{-1}$ in a STA449C integrated thermal analyzer. The sintered disk samples were characterized by XRD (D/max-γβ X-ray diffractometer with 40mA and 40kVv, CuKR radiation, Japan) for the determination phase transformation. Morphology of the sintered bodies was observed using a JSM-6700F scanning electron microscope (Japan) at an accelerating voltage of 20 kV.

3. Results and discussion

3.1 DTA-TG analyses

Fig.1 shows TG-DTA curves of ceramic sample. It is seen that there are three endothermic valleys at 129.3, 696.2 and 911.6 °C for ceramic sample. The endothermic valley at129.3 indicates that the surface absorbing water is vaporized, and endothermic valley at 696.2 and 911.6 °C indicates that the structure water of ceramic sample is released. As can be seen, the exothermic peaks of ceramic sample is detected at 453.9, 727.4 and 862.9 °C. The exothermic peaks at 453.9 °C corresponds to convert WKT into amorphous metakaolin, and
the exothermic peaks at 727.4 and 862.9 °C corresponds to chrysotile converting into forsterite. The thermal analyses results indicate that there is not solid phase reaction among ceramic sample below 1000°C.

![Fig.1](image1.png)

**Fig.1** The DTA curves of the physical raw materials mixtures.

### 3.2 XRD analysis phase transitions

Fig.2 shows XRD patterns of WST treated at various temperatures (25, 650,750, 850, and 1000 °C). It is seen from Fig.2 that Lizarsi is the main crystalline phase below 650 °C, which indicates that there is not the release of structure water in WST corresponding to the result of TG-DTA. From the same figure, it is seen that the forsterite becomes the main crystalline phase, which indicates that WST starts to release the structure water corresponding to the results of TG-DTA. When temperature is increased to 1000 °C, forsterite and enstatite become the main crystalline phases.

![Fig.2](image2.png)

**Fig.2** XRD pattern of WST treated at various temperatures (25, 650,750, 850, and 1000 °C.)
Fig. 3 shows XRD patterns of WKT treated at various temperatures (25, 350, 600, 1000, and 1200 °C). It is seen from Fig. 3 that quartz and kaolinite are the main crystalline phase below 350 °C. From the same figure, it is seen that quartz becomes the main crystalline phase when temperature increase from 600 to 1000 °C. This indicates that kaolinite in WKT is converted into amorphous metakaolin corresponding to the results of TG-DTA. When temperature is increased to 1200 °C, mullite and quartz become the main crystalline phases.

![Fig.3 XRD pattern of WKT treated at various temperatures (25, 350, 600, 1000, and 1200 °C).](image)

Fig. 3 XRD pattern of WKT treated at various temperatures (25, 350, 600, 1000, and 1200 °C).

Fig. 4 show XRD patterns of ceramic samples sintered at various temperatures (800, 900, 1100, 1200, 1300 and 1350 °C). It is seen from Fig. 4 that quartz, forsterite and enstatite are the main crystalline below 1200 °C. When temperature is increased to 1350 °C, the cordierite becomes the main crystalline phase. This result indicates that the cordierite forms at about 1350 °C with the interaction of forsterite, enstatite, mullite and quartz.

![Fig.4 XRD pattern of ceramic sample sintered at various temperatures (800, 900, 1100, 1200, and 1350°C).](image)

Fig. 4 XRD pattern of ceramic sample sintered at various temperatures (800, 900, 1100, 1200, and 1350°C).
3.3 Ceramic appearance and microstructure

Fig. 5 shows appearance (a), SEM micrograph (b), and cordierite compositions (c) of ceramic sample sintered at 1350 °C. It is seen from Fig. 5 (a) that the cordierite ceramics is undeformed. It is seen from Fig. 5 (b) that the cordierite shows the typical rhombic system, which has the compositions of O, Al, Si and Mg (In Fig. 5c).

Fig. 5 Appearance (a), SEM micrograph (b), and cordierite compositions (c) of ceramic sample sintered at 1350 °C for 3 h.

4. Conclusion

The cordierite ceramics has been successfully synthesized by using raw materials including WST, WKT, and alumina. The XRD results showed that the synthesized material sintered at 1350 °C for 3 h is formed the cordierite phase. SEM observation shows that the cordierite with the compositions of O, Al, Si and Mg shows the typical rhombic system.

Acknowledgments

The authors are grateful for support of the key subject of Shanghai Municipality (S30109) and Shanghai Science and Technology Commission (10dz1205302).

5. References


Садржај: Кордијеритна керамика је синтетисана из три различита јединиња: отпадног хидратисаног магнезијумовог силиката из рудника, каолина и алиумина. Формирање кордијерита је постигнуто рекционим синтеровањем на 1350 ºC током 3 сата. Синтетисани кордијерит је карактерисан рендгенском дифракционом анализом, диференцијалном термијском анализом и EDS-SEM анализом. Рендгенска анализа је указала на кордијерит са типичном ромбичном структуром као главном фазом, док је EDS-SEM указао на јединење састојено из O, Al, Si и Mg.

Кључне речи: отпадни хидратисани силикат магнезијума, отпадни каолин, кордијерит, синтеровање, реакција у чврстој фази.