CHEMICAL REACTION BETWEEN POTASSIUM ALUMINOSILICATES AND AGGREGATES AT DIFFERENT TEMPERATURE

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ABSTRACT

Kalsilite/kaliophilite ($KAlSiO_4$, KAS) could be used in saggars for the calcination of $Li(Ni_xCo_yMn_z)O_2$ ternary battery materials because kalsilite has high melting point (1750℃) and could be chemically resistant to ternary battery materials. However, the compatibility of KAS with the commonly used aggregates in the saggars is not clear. In this work, KAS was synthesized using potassium carbonate (K_2CO_3), silica and alumina. Then the as-synthesized KAS fine powder was mixed with four kinds of fine powders (alumina, mullite, cordierite and magnesia-alumina spinel) respectively to magnify the possible reactions. The mixtures were fired at 1370℃ and subsequently examined by means of XRD and SEM to investigate the reaction between the KAS fine powder and various aggregates.

Keywords: saggars for ternary battery firing; kalsilite; aggregates; reaction

INTRODUCTION

$Li(Ni_xCo_yMn_z)O_2$ (LNCM) ternary battery materials has been widely applied in portable devices and electric vehicles as an efficient energy storage medium because of its high specific capacity, low cost, long cyclic life, and both structural and thermal stability[1]. LNCM can be fabricated via multiple approaches such as solid state, co-precipitation, sol-gel and spry drying. Industrially, through firing appropriate mixtures of raw materials at elevated temperature, LNCM is prepared with great amount at low cost[2].

Corundum and mullite saggars have been industrially used in the calcination of LNCM. However, severe corrosion takes place from external to internal of saggars, causing their average service life pretty short. At about 1000 ℃, the normal calcination temperature, LNCM precursor penetrates into saggars and produces multiple liquid products, which would infiltrate more easily[3]. The resulted corrosion products, which have obviously distinct thermal expansion coefficients compared with surrounding saggars materials, generate cracks during the periodic cooling-heating circles, and lead to spalling off of the outer layers. Besides, low-quality LNCM materials are produced owing to the consumption and contamination in the process of sintering. Therefore, it is a new solution to develop new types of saggars materials for the LNCM calcination.

Kalsilite/kaliophilite ($KAlSiO_4$, KAS) is stable at high temperatures and alkali-rich environments partially due to its high melting points at 1750 ℃[4]. Besides, KAS may not react with lithium compounds because K and Na elements are in the same group in periodic table and their compounds possess similar chemical property. Therefore, KAS is a promising candidate material used as saggars for sintering of LNCM ternary battery materials. In addition, it's worth noting that the thermal expansion coefficient of KAS is $20 \cdot 10^{-6}$ ℃$^{-1}$ ($16 \cdot 10^{-6}$ ℃$^{-1}$ and $28 \cdot 10^{-6}$ ℃$^{-1}$ along a/b and c axis, respectively), which is much higher than that of corundum and mullite[5]. Therefore, mixing of KAS and common aggregates at appropriate ratio so as to facilitate micro-crack toughening is the critical issue in this topic. But more importantly, possible reactions between KAS and various aggregates such as corundum, mullite, cordierite and magnesia-alumina spinel should be verified in the first place.

EXPERIMENTAL

For the preparation of KAS, K_2CO_3, commercial alumina (Al_2O_3: 98.9%) and silica powders were mixed in a molar ratio of 1:1:2 in a rotary mill for 12 hours, using corundum balls of 10mm as the milling media with a balls/powder weight ratio of 5/2. In this study, ethanol was used as liquid medium. The slurry was dried in a chamber at 110 ℃ and then compacted to cylinders (diameter 36mm, weight approximately 25g, height approximately 10mm) at 50 MPa with a uniaxial press. After sintered at 1200 ℃ for 8 hours, the specimens were crashed and sieved to obtain KAS powders with a particle size below 200 mesh.

The synthesized KAS powder was mixed with corundum, mullite, cordierite and magnesia-alumina spinel powders (size below 200 mesh) in various weight ratios as shown in Tab. 1, respectively. The mixing process was carried out for 1 hour, using a vibratory Spex 8000 mixer to achieve a better homogenization. For each group, 4g of the mixture and a stainless-steel ball (12.7 mm in diameter) were placed into a

stainless-steel cylindrical vial (40 mm in diameter and 40 mm in height) before mixing. Then, the mixtures were compacted into a strip (length and width 4 mm, height 38mm), at 12MPa with a uniaxial press. The specimens were sintered at 1370 ºC for 3h in an electric chamber furnace.

Tab. 1: Composition of mixtures of KAS and various aggregates powder.

Raw material content (g)		
KAS	$Al_2O_3/3Al_2O_3·2SiO_2/$ $2MgO·2Al_2O_3·5SiO_2/MgO·Al_2O_3$	Sample
4	0	K4
0	4	A4/M4/C4/S4
1	3	A3/M3/C3/S3
2	2	A2/M2/C2/S2
3	1	A1/M1/C1/S1

Reaction products of the KAS powders and various aggregates powders were examined with X-ray powder diffraction (XRD: Philips X' Pert Pro)[6]. Micro structural analysis of the samples after calcinations were carried out with scanning electron microscopy (SEM: ΣIGMA™ HD)[7].

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of synthesized KAS. After firing at 1200 ºC for 8 hours, almost all peaks are related to orthorhombic $KAlSiO_4$.
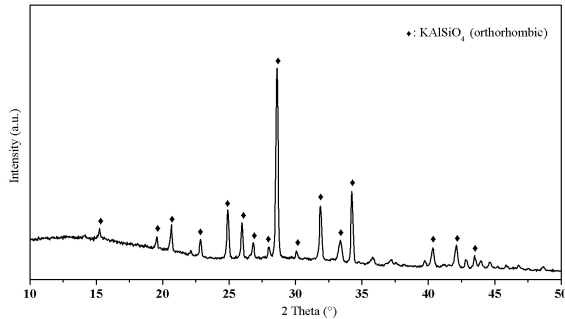

Fig. 1: X-ray diffraction patterns of synthesized KAS ($KAlSiO_4$: powder diffraction file No. 33-0989).
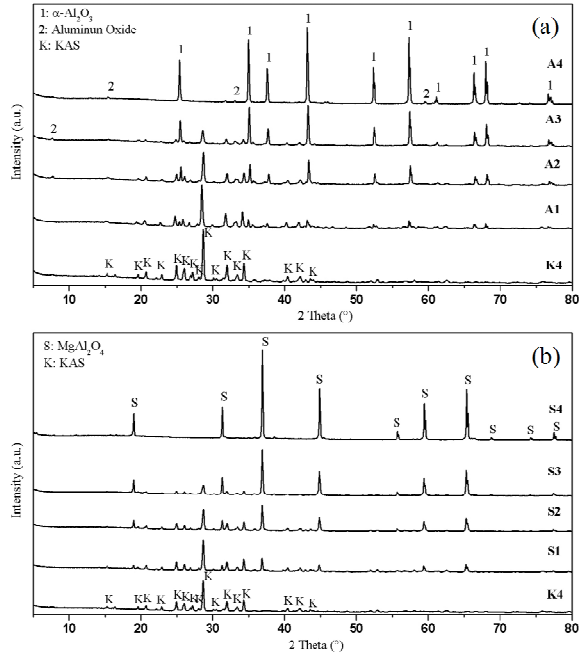

Fig. 2: X-ray diffraction patterns of corundum mixtures (a) and magnesia-alumina spinel mixtures (b) after heat treatment at 1370 ºC for 3h (1, $α-Al_2O_3$: powder diffraction file No. 74-1081; 2, aluminum oxide: powder diffraction file No. 51-0769; K, $KAlSiO_4$: powder diffraction file No. 33-0989; S, $MgAl_2O_4$; powder diffraction file No. 82-2424).

As seen from Fig. 2, after firing at 1370 ºC for 3h, no reaction products were detected when the corundum or magnesia-alumina spinel powder was added into KAS in various ratios. $α-Al_2O_3$ and aluminum oxide were the main phases of the sintered corundum powders (Fig. 2a, A4). With the addition of corundum into KAS (from A1-A3 in Fig. 2a), intensity of $α-Al_2O_3$ peaks gradually increase while the peaks corresponding to $KAlSiO_4$ declined accordingly. Similarly, in the mixtures of magnesia-alumina spinel and KAS, peaks of $MgAl_2O_4$ experienced an upward trend while that of KAS showed the opposite (Fig. 2b, S1-S3). Therefore, corundum and magnesia-alumina spinel may be used in KAS system due to their good adaptability.

Fig. 4: Scanning electronic microscopy micrographs of the polished sample surface (Corundum mixtures (A2) before (a) and after (b) heat treatment and magnesia-alumina spinel mixtures (S2) before (c) and after (d) heat treatment).
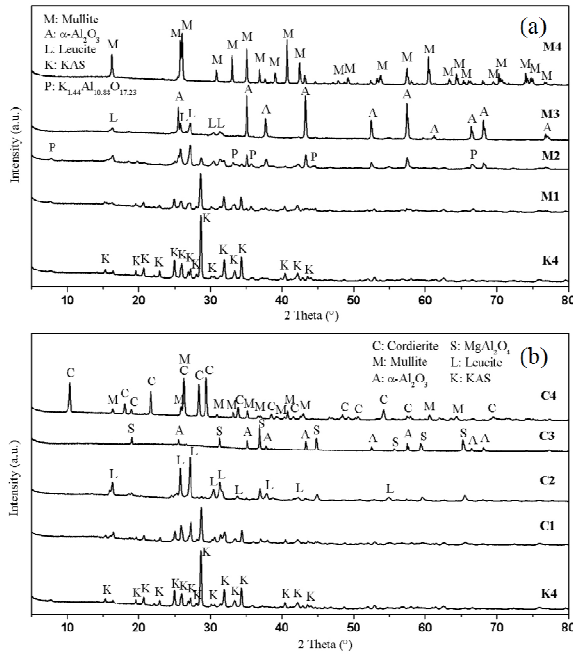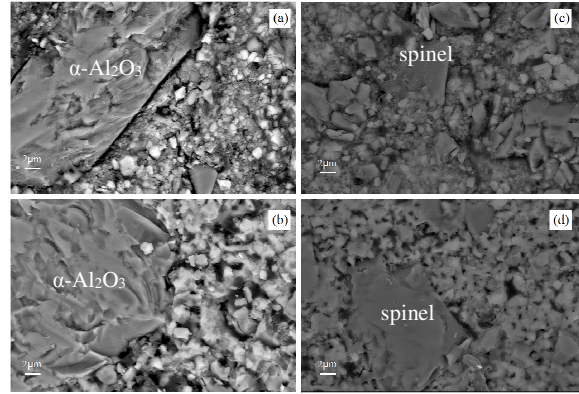
Fig. 3: X-ray diffraction patterns of mullite mixtures (a) and cordierite mixtures (b) after heat treatment at 1370 °C for 3h (M, mullite ($A_6Si_2O_{13}$): powder diffraction file No. 15-0776; A, α-Al_2O_3: powder diffraction file No. 74-1081; L, leucite ($KAlSi_2O_6$): powder diffraction file No. 71-1147; K, $KAlSiO_4$: powder diffraction file No. 33-0989; P, $K_{1.44}Al_{10.88}O_{17.23}$: powder diffraction file No. 84-0819; C, cordierite ($Mg_2Al_4Si_5O_{18}$): powder diffraction file No. 85-1722; S, $MgAl_2O_4$: powder diffraction file No. 82-2424).

Fig. 3 shows the XRD patterns of mullite mixtures (a) and cordierite mixtures (b) after calcining at 1370 °C for 3h. In Fig. 3a, with the addition of mullite into KAS, intensities of peaks of KAS decrease and small amount of $K_{1.44}Al_{10.88}O_{17.23}$ generates (Fig. 3a, M1). Further increase of mullite addition to the same amount of KAS (Fig. 3a, M2) allows the generation of α-Al_2O_3 and leucite. When the content of mullite is higher than that of KAS (Fig. 3a, M3), peaks of KAS completely disappear whereas intensities of α-Al_2O_3 and leucite are observed. Fig. 3b demonstrates the reaction behavior of cordierite and KAS at various ratios. It's seen from the figure that different reaction products generate at different ratios. It's worth noting that only sample C3 melt during calcination process, indicating that intermediate products with low melting point were generated. In summary, mixing of mullite and cordierite with KAS allows the generation of different reaction products in various ratios. Therefore, mullite and cordierite may not fit in with KAS because of the reaction behaviors.

The scanning electronic microscopy micrographs of corundum mixtures and magnesia-alumina spinel mixtures before and after calcinations for 3h at 1370 °C are presented in Fig. 4. It can be seen from Fig. 4 that the gray α-Al_2O_3 grains and the bright white $KAlSiO_4$ granulum are distributed separately in the samples (Fig. 4(a), (b)), which is similar for magnesia-alumina spinel mixtures (Figs. 4a and b). After calcinations, $KAlSiO_4$ granulum agglomerates and surrounds the α-Al_2O_3 grains and spinel grains. It's worth noting that in both systems the bond between grains and $KAlSiO_4$ grows stronger after firing process. No reaction products are detected in grain boundaries after calcination, which is consistent with the XRD results (Fig. 2).

Fig. 5 shows the SEM images of mullite mixtures (M3) before and after heat treatment. It's seen from Fig. 5b that mullite grains react with $KAlSiO_4$ granulum completely after calcination, forming needle-like α-Al_2O_3 grains.
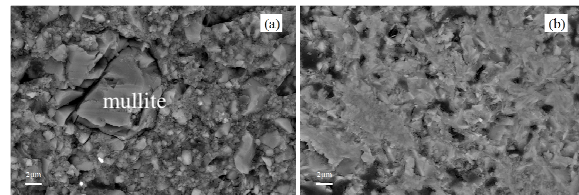

Fig. 5: Scanning electronic microscopy micrographs of the polished sample surface (mullite mixtures (M3) before (a) and after (b) heat treatment).

Fig. 6 shows the SEM images of cordierite mixtures (C3) before and after heat treatment and the appearance of the molten sample. Cordierite grains react with $KAlSiO_4$ granulum to generate α-Al_2O_3 and spinel. During firing process, liquid phase was generated and results in big pores in the sample (Fig. 6c).
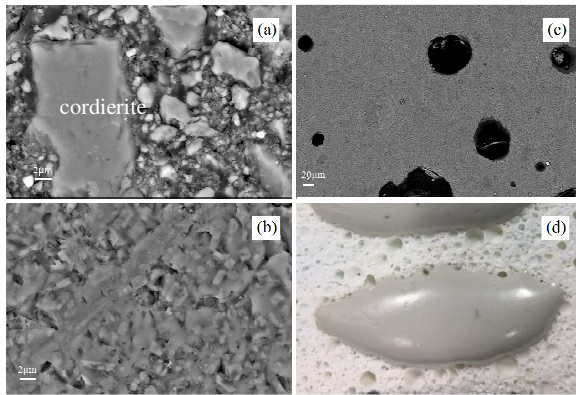
Fig. 6: SEM micrographs of the polished sample surface (cordierite mixtures (C3) before (a) and after (b) and (c) heat treatment); (d): diagram of sintered sample (C3).

CONCLUSIONS

KAlSiO$_4$ was synthesized through solid state reactions. The reaction behaviors between KAS and various aggregates (corundum, mullite, cordierite and magnesia-alumina spinel) were studied after firing at 1370 ℃ for 3h. Based on the XRD results, corundum and magnesia-alumina spinel are promising materials to be used with KAS due to their stability in KAS in various ratios. Conversely, mullite mixtures and cordierite mixtures generate different reaction products in various ratios after firing. Therefore, mullite and cordierite may not fit in with KAS. The SEM results show that corundum and magnesia-alumina spinel grains do not react with KAS after firing while mullite and cordierite react with KAS to form different reaction products.

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