QUANTITATIVE PHASE ANALYSIS RESULTS EVALUATION OF SINTERED MULLITE BY RIETVELD FULL SPECTRUM FITTING

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Abstract: Mullite, $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}(0.17 \leqq x \leqq 0.59)$, is a serials of non-stoichiometric compounds in Al_2O_3-SiO_2 system without certain chemical compositions, which also cause the different X-ray diffraction patterns of mullite. Therefore, 5 different mullite reference cards were given in the databank of commercial software of Siroquant. When performing quantitative phase analysis of mullite, the test results are always different from each other if a mullite reference card or combination of them was selected, and meanwhile, amorphous contents show much more difference from each other. Actually, for a sample with the same scanning, the glass phase content shall be certain because of it does not depend on the crystal orientation. This may indicate the difference between the used mullite reference and actual mullite structure of sample affect the analysis results significantly. With the aim to overcome this problem, phase analysis of sintered mullite has been done by Siroquant software using ZnO a reference material, and the minimum total relative standard deviation (TRSD) method based on least squares criterion principle was used to evaluate the test results. Results show that the most possible mullite structure of samples could be determined by using the TRSD method, and meanwhile, calculated amorphous contents are close to that derived by chemical method.

Key Words: Amorphous, Mullite, X-Ray Diffraction Spectrum, TRSD

1. INTRODUCTION

The amorphous phases and the imperfect crystal (here in after referred to as amorphous) all are the incomplete lattice solid materials. There are many methods for determination of amorphous phase, such as infrared spectrum [1], selective dissolution [2], optical microscope [3] and X ray diffraction spectroscopy (hereinafter referred to as XRD) method [4-6]. The factors of preferred orientation, micro absorption effect, peak overlap, sample preparation and peak dispersion may cause errors in the measurement results of amorphous phase by XRD method [7-9]. The quantitative phase analysis by Rietveld method of whole pattern fitting of the X-ray powder diffraction data, currently, is a very important and common method. The essence of Rietveld structure refinement is an iterative error correction between the single crystal parameters of the known crystal and the measured polycrystalline powder parameters. Obviously, Rietveld method cannot fit the amorphous phase and the unknown phase. There are many commercial software used Rietveld method for qualitative analysis and employed the second iteration method to calculate the amorphous phase by spiking phase methods. Siroquant is one of the commercial softwares which based on Rietveld principle. Some necessary known crystal structure models and structural parameters are input into Siroquant, and then the poly-crystal diffraction spectrum is calculated from the set parameters, a sum of squares of errors between the fitted curve and the experimental one would be derived. Changed the input parameters and repeated the fitting again until the minimum sum of squares of errors was gained, and the corresponding phase contents results would be given as the final results. The content of amorphous phase is determined by spiking ZnO in Siroquant.

Mullite, corundum, quartz, and amorphous phase are main phase compositions of sintered mullite using natural raw materials belong to Al_2O_3-SiO_2 system [10]. Mullite is rare with ideal chemical formula $(Al_2O_3)_3(SiO_2)_2$ (hereinafter referred to as A_3S_2). Most of them have similar crystal structure with different chemical composition, which results in a difficulty for whole spectrum fitting. As a consequence, there is still no report on the quantitative phase analysis of mullite by XRD method.

In this paper, the Siroquant software was used for quantitative phase analysis of sintered mullite. At the same time, ZnO was introduced as a spiking phase to assist the calculation of amorphous phase. The relative standard deviation minimization principle is established to evaluate the test results and propose the most possible crystal structure of mullite in sample and amorphous phase content.

2. EXPERIMENTAL PROCEDURE

Mullite samples are firstly grinded into powder finer than 0.088mm for sample preparation. Take grinded mullite powder and ZnO with the ratio of 10:1 precisely and mix them together well to ensure good homogeneity. Take the 2.5g mixture and press it into disc shape. Sample preparation was finished by using YXCY-80 Semi automatic press (Ji'nan Kade analytical instrument factory，the patent head of boric acid wrapping) with the pressure of 410 kN. ARL9900 X-Ray Workstation coupled with X-ray spectrometer (Thermo Scientific Co.) was used to perform quantitative phase analysis of different sintered mullite samples. X-ray spectrometer used a 4.2kW X- ray tube with working voltage of 40kV and current of 40mA. For each sample, scanning from 8°～80°with a step of 0.1°sec. Siroquant quantitative analysis software was employed to carry out data analysis. One of the key points to process the calculation of phase contents is to set the possible crystal structure. Considering the uncertainty of mullite structure and the 5 available reference patterns of mullite in Siroquant quantitative analysis software databank, 31(see following) different reference combinations(RC) of them were fully input to the software as the initial conditions to carry out analysis.

Tab. 1 31 mullite reference compositions

RC	Combinations	RC	Combinations
1	M1	16	M1+ M2+ M3
2	M2	17	M1+ M2+ M4
3	M3	18	M1+ M2+ M5
4	M4	19	M1+ M3+ M4
5	M5	20	M1+ M3+ M5
6	M1+ M2	21	M1+ M4+ M5
7	M1+ M3	22	M2+ M3+ M4
8	M1+ M4	23	M2+ M3+ M5
9	M1+ M5	24	M3+ M4+ M5
10	M2+ M3	25	M2+ M4+ M5
11	M2+ M4	26	M1+M2+ M3+ M4
12	M2+ M5	27	M1+M2+ M3+ M5
13	M3+ M4	28	M1 + M3+ M4+M5
14	M3+ M5	29	M2+ M3+ M4+ M5
15	M4+ M5	30	M1+M2+ M4+ M5
		31	M1+M2+ M3+ M4+ M5

Assuming that 5 different mullite reference patterns as M1(A_3S_2), M2($A_3S_{1.92}$), M3($A_3S_{1.83}$), M4($A_3S_{1.71}$) and M5($A_3S_{1.56}$), respectively, then the total RC could be calculated according to the following equation. The detailed 31 RC are showed in table 1.

$$T_{RC} = C_5^1 + C_5^2 + C_5^3 + C_5^4 + C_5^5 = 31 \qquad (1)$$

3. RESULTS AND DISCUSSIONS

3.1 SYNTHESIS OF TOTAL RELATIVE STANDARD DEVIATION

The least squares method is a mathematical optimization technique. It searches for the best function of the data by minimizing the sum of squares of errors. For every sample after a scanning, a certain XRD pattern will be derived. Different analysis results would be got with different mullite reference pattern or their combinations according to Table 1.

The relative deviation should be used instead of absolute error in mixing square for the difference of amorphous phase and spiking phase, due to the spiking phase content and the fitting error is based on the results of the first spiking fitting, and the content of amorphous phase is calculated after error analysis. All crystal phases (including spiking phase) contents in a mullite sample and their errors should be analyzed by Siroquant first, because of uncertainty of the mullite composition, and then all crystal phases (excluding spiking phase) and amorphous contents together with their errors are calculated by Siroquant. The relative errors of all crystal phases and amorphous phase can be calculated and the total relative error of every combination can be composed easily.

Each calculation would give errors of each found phase if a pre-set ZnO content was input into the Siroquant software, and then the total relative standard deviation can be calculated by equation (2).

$$TRSD = \sqrt{\sum M_{rsd}^2 + C_{rsd}^2 + A_{rsd}^2} \qquad (2)$$

TRSD means total relative standard deviation, $\sum M_{rsd}^2$ means the sum of relative standard deviation of each mullite reference pattern of each calculation according to Table 1, C_{rsd} means the relative standard deviation of corundum phase, A_{rsd} means the relative standard deviation of amorphous. The combination with the minimum total relative error is the composition of mullite and its contents of crystals and amorphous are the contents which we want know, by the least square rule.

Tab.2 TRSD of different scanning of a sample

RC	scan-1	scan-2	scan-3	scan-4
1	21.53	22.15	21	21.84
2	14.4	14.5	15.6	14.6
3	24.1	24.4	25.4	21.8
4	26.7	25.09	25.24	24.64
5	23.44	23	22.84	22.48
6	49.35	49.29	50.18	48.71
7	100	100	100	100
8	52.8	50.5	50.9	48.6
9	50.6	49.19	49.73	48.02
10	60.2	59.91	61.41	59.15
11	51.93	49.35	50.33	47.07
12	43.49	41.96	42.81	39.98
13	58.9	55.2	55.7	52.4
14	54.05	53.75	54.2	51.83
15~31	>100	>100	>100	>100

3.2 EFFECT OF CRYSTAL ORIENTATION ON THE TEST RESULTS

In order to make sure whether the crystal orientation has some effect on the quantitative phase analysis results of mullite, a specific sample A has been scanned for four times.

The sample would be re-installed into sample support after the former test to change the crystal orientation. The calculated TRSD was shown in Table 2.

It is obvious that the each TRSD of calculations using RC number from 15 to 31 as initial condition is bigger than 100%, which may indicate that the big difference between the selected RC and actual mullite structure. However, calculation results are much better using RC of 1 to 14. This suggests that the actual phase compositions of the tested sample are similar as that of RC used. Furthermore, it is easy to find out that the TRSD of calculation result with RC 2 is the minimum compared with others according to following Fig.1. Meanwhile, the TRSDs of a sample calculated through different scanning are almost same with each other, which may imply that the orientation of sample has little influence on the phase composition analysis results.

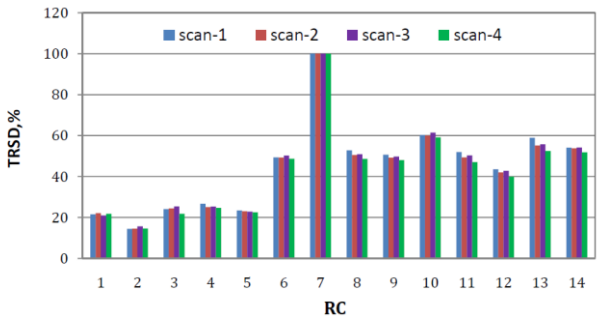

Fig.1 TRSD of a specific sampe with different scannings

3.3 APPLOCATION OF TRSD METHOD ON DIFFERENT SAMPLES

So as to that the crystal orientation has slight effect on the test results of mullite by Siroquant and using TRSD method, this technique has been proposed to different samples. The other mullite samples marked by B and C together with A have been analyzed just by one scanning.

Tab.3 TRSD of different scanning of a sample

RC	Sample-A	Sample-B	Sample-C
1	21.53	13.96	23.10
2	14.40	13.92	21.60
3	24.10	14.30	25.50
4	26.70	12.65	18.90
5	23.44	11.73	18.90
6	49.35	33.22	53.20
7	100.00	100.00	100.00
8	52.80	20.71	36.00
9	50.60	21.70	39.20
10	60.20	34.35	58.40
11	51.93	18.15	33.20
12	43.49	17.92	32.80
13	58.90	21.66	38.40
14	54.05	23.19	42.40
15~31	>100	>100	>100

TRSDs of each sample using different RC have been calculated and shown in Table 3. It is obvious that the TRSDs sample A, B and C calculated using RC number from 15 to 31 are all bigger than 100%. This is similar as that of sample A with different scanning, which indicates that it is impossible for both sample A, B and C to contain the mullite structure combinations of RC number from 15 to 31. However, TRSDs of

all samples calculated using less than 3 mullite reference combination, i.e. the RC number from 1 to 14 are much smaller. For each sample, a minimum TRSD could be derived and shown in Fig.2. For sample A, it seems that the RC of No.2 which indicates only one most possible mullite structure is M2, the $A_3S_{1.92}$. While for sample B and C, their most possible mullite structure are suggested to be the same of M5($A_3S_{1.56}$). In fact, according to Fig.2, it is certain that the minimum TRSD method could indicate the most possible mullite structure of a sample.

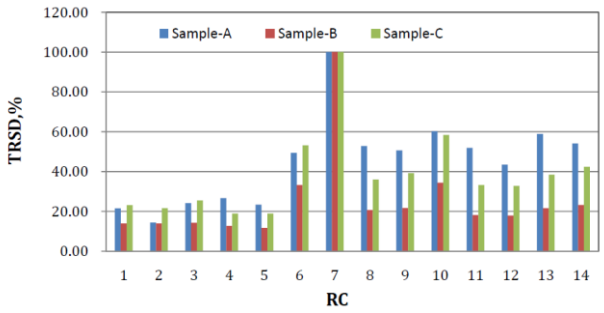

Fig.2 TRSD of different sampes with one scanning

It is believed that no matter what the actual mullite structure of a tested sample, single or their combinations, the minimum TRSD method has the ability to propose the most possibility.

2.4 TESTED AMORPHOUS CONTENT COMPARED WITH OTHER METHODS

The amorphous contents of three different samples determined by XRD (using the minimum TRSD method) and chemical analysis according to the document [2] are listed in Table 4.

Tab.4 Amorphous contents of different samples by different methods

Sample No.	Sample- A	Sample -B	Sample -C
Mullite composition	$A_3S_{1.92}$	$A_3S_{1.56}$	$A_3S_{1.56}$
amorphous Contents by XRD	29.0%	29.4%	27.8%
amorphous Contents by Chemical analysis	19.5%	20.2%	16.4%

The amorphous contents of all samples by XRD method are about around 50% higher than that of chemical analysis. This may be caused by the coating defect. In fact, the crystal particles are covered by amorphous, defect and/or microcrystalline ones, and therefore, the amorphous particles are rayed before crystal by X-ray, and higher diffraction intensity can be got than crystal component.

3. CONCLUSIONS

(1) Crystal orientation has slight effect on the phase compositions analysis by XRD method.
(2) The most possible mullite structure or their combinations of tested samples could be determined by the minimum TRSD method, as well as each crystal phase content.
(3) The amorphous content of a sample could also be determined directly by XRD method using a spiking reference phase, which is also close to that derived by traditional chemical method.

4. References

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