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The application of the *in situ* high-temperature X-ray diffraction quantitative analysis

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Abstract

An extending RQA standardless method is applied to *in situ* high-temperature quantitative analysis of Cu_2O–Al_2O_3–SiO_2 pseudo-ternary system. By carrying out the refinement of the *in situ* high-temperature XRD data according to the designed uniform refining strategy, we analyzed the influences of the refined variables on the analytical results such as the phase fraction and the residuals. It indicates that the thermal diffuse scattering function gives a satisfactory fitting for the background. The refinements of temperature factors of atoms and lattice parameters of unit cells are the prerequisite for the refinements of the other structure factors, and the preferred orientation can be effectively reduced in the RQA method for anisotropic crystalline phases. The reliable results were obtained and the precision has reached 0.1–2.3%.

Keywords: Oxide materials; Quenching; High-temperature X-ray diffraction

1. Introduction

Quantitative X-ray powder diffraction (QXRPD) is applied to a wide range of materials field, from basic science research to technological studies and industrial quality control. Theoretically, QXRPD is the most powerful technique for the quantitative analysis of multiphase crystal powder system, which is based on the fact that the integrated reflecting intensity diffracted by a crystalline phase is proportional to its phase abundance in the multiphase powder. However, significant advances had not occurred for QXRPD method which is applied in XRD pattern of the complex sample system until the Rietveld method of quantitative analysis (RQA) was used in the last 20 years [1–6]. Moreover, the combination of RQA and the reference intensity ratio method (RQA–RIR) [7,8] cannot only eliminate the deviation of the analysis result of crystalline phase caused by the amorphous phase, but also determine the content of the amorphous phase of which the accuracy can even reach 1%. In some cases, however, the RQA standardless method must be applied when there is no suitable internal standard or the QXRPD method must be carried out freely from the interference of the other phases. Esteve et al. [9] have reported the determination results of mixtures of eight crystalline phases by the RQA standardless method. The results indicated that their deviations are between 0.2 and 9.6% in which the larger errors related to the larger residuals (R_p and R_{wp}).

The quantitative phase analysis of high-temperature system is an important procedure in the determination of high-temperature phase diagrams. In general, the components of the high-temperature system are frozen by the quenching method and then analyzed by the conventional QXRPD method at room temperature. Sometimes, however, it is impossible to freeze the phases in the case of the high-temperature system to room temperature by conventional methods due to the very rapid phase transformation in some complex systems during the quenching procedure. The situation was encountered in the Cu_2O–Al_2O_3–SiO_2 pseudo-ternary system, which consists of polycrystalline phases and molten liquid phase at 1150 °C. The quantitative analysis of the phases in different composition is the key to determine the phase regions of the isothermal phase diagram. As we know, the character of phase equilibrium of a system closely relates to its composition. So the addition of internal standard

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Table 1
Chemical composition of the three Cu_2O–Al_2O_3–SiO_2 samples (mol%)

Sample	SiO_2	Al_2O_3	Cu_2O
1	61	34	5
2	75	19	6
3	81	14	5

crystalline phase for RIR method will certainly change the feature of phase equilibrium. Therefore, the RQA standardless method rather than the RQA–RIR method can only be applied in the quantitative phase analysis of the high-temperature systems. In this paper, the RQA standardless method was performed to some compositions of the Cu_2O–Al_2O_3–SiO_2 pseudo-ternary system, and some influences of variables on the accuracy in RQA was discussed in detail.

2. Experimental procedure

2.1. Preparation of samples

Three compositions of Cu_2O–Al_2O_3–SiO_2 samples are prepared as listed in Table 1. The starting materials are the gels of their compositions made of hydrates of aluminum and copper nitrates and tetraethyl orthosilicate in ethanol with added concentrated HNO_3 as catalyst using sol–gel method [10]. The crude sample powders obtained from the dried gels were ground and pressed into pellets. After a sequentially "slow" heating at a rate of 3–5 °C/min to 600 °C and then a "quick" heating at a rate of ∼15 °C/min to 1150 °C in a platinum crucible for 12 h, the sample pellets were quenched in cold water following the sample drying at 110 °C for 2–3 h, and finally crushed into fine powder. Because Cu_2O would be oxidized when the temperature decreased to be lower than 1026 °C [11], the quenching process should be as fast as possible.

2.2. XRD data collection and the identification of crystalline phases

The XRD patterns were collected on a Philips X'-Pert MPD diffractometer with X'Celerator detector using Cu Kα radiation (40 kV, 40 mA). A slurry sample was prepared from the ground sample and suitable amount of ethanol was mounted on a platinum strip which served as horizontal sample holder as well as heater attached with Anton Parr HTK 2000 high-temperature controlling units which were used for *in situ* high-temperature XRD measurements. Firstly, the XRD pattern at room temperature was recorded and then the sample was heated to 1150 °C at a rate of 30 °C/min. The XRD patterns were recorded within 10–110° (2θ) with a step size of 0.0167° (2θ) and a step time of 30 s after annealing at the temperature for 10 min.

The crystalline phases of the quenched powder samples were identified with JCPDS, and the XRD peaks were indexed with the standard structural models. It appears by comparison that for an identical composition the phases in high-temperature state are generally the same as the main phases in the quenched sample. So, the initial structural models of high-temperature XRD pattern in Rietveld method adopted the identification results of the crystalline phases of the same composition of quenched samples.

2.3. Mathematical basis and strategy of refinement for the high-temperature structure

In this paper, RQA is carried out by Rietveld refinement using GSAS software package [12]. According to the mathematical principle, the total calculated powder diffraction profile intensity (I_c) at any point in a diffraction pattern is contributed from the sum of the reflection intensities of all crystalline phases ($\sum_p S_p Y_p$) and the intensities of background and diffuse scattering ($I_b + I_d$). Its mathematical expression is as follows:

$$I_c = (I_b + I_d) + \sum_p S_p Y_p \quad (1)$$

In the refining process, the contribution of ($I_b + I_d$) can be simulated from the suitable selected empirical equations and experimental model which are suited in the GSAS. Meanwhile, ($\sum_p S_p Y_p$) are the sum of the arithmetic product of the phase fraction for phase p (S_p) and the Bragg diffraction profile intensity (Y_p) of crystalline phase p in the sample, where S_p can be converted into the weight fraction (W_p) of each phase of multiphase mixture in the RQA:

$$W_p = \frac{S_p m_p}{\sum_{p=1}^{N_p} S_p m_p} \quad (2)$$

where the unit cell weight of the pth phase (m_p) can be calculated from the optimization result of crystal structure.

The process of RQA method is based on the least square theory. In general, the expressions for the calculated values corresponding to the set of crystallographic observations are transcendental and thus the least squares minimization function is non-linear and the process is iterative. The minimization function can be expressed as formulas (3) and (4) which are the residuals for the Bragg contribution (R_{pb}) and the weight Bragg contribution (R_{wpb}), respectively, and measures for the quality of the minimization

$$R_{pb} = \frac{\sum |I_o - I_c| \times |I_o - I_b| / \sum I_o}{\sum |I_o - I_b|} \quad (3)$$

$$R_{wpb} = \sqrt{\frac{\sum w[(I_o - I_c)(I_o - I_b)/I_o]^2}{\sum w(I_o - I_b)^2}} \quad (4)$$

where I_o is the total profile intensity of observation after normalization and w is a weight assigned to each diffraction.

Usually, it is not necessary to refine the structural factors and lattice parameters in the conventional RQA analysis. However, in the *in situ* high-temperature XRD–RQA, the selected crystal structure models which are often the room temperature crystal structures are just to be used as the initial models of the high-temperature crystal structure. In fact, therefore, the primary procedure of the *in situ* high-temperature RQA is the multiphase structural refinement, in which the lattice parameters and the temperature factors of the atoms in the structure have been changed at high temperature and finally the weight fraction as well as the phase fraction of each phase is concomitant with the refinement results.

In order to obtain a convergence result till R_p/R_{pb} and R_{wp}/R_{wpb} reaching the satisfied minimum, it is necessary to design the refining strategy, namely the respective fitting combinations of variables or the sequence of the combinations in the refinement, according to the importance of the factors influencing on the residuals. The main procedures of the refining strategy of the high-temperature RQA refinement in this paper are as follows:

(1) successively refining the background and diffuse scattering function including the amorphous phase in the sample, and the zero point shift of the pattern to correct the systemic deviation;
(2) refining the phase fractions of all the crystalline phases, respectively;
(3) refining the isotropic temperature factors of the atoms in different crystalline phases, respectively, in which the temperature factors of all atoms in every crystalline phase are usually restrained;
(4) refining the lattice parameters of all the crystalline phases, respectively;
(5) refining the preferred orientation of mullite.
(6) refining the peak profile parameters of pseudo-Voigt II profile function, in which the identical profile function parameters of all the crystalline phases are restrained;
(7) refining the absorption factor if necessary.

The above refining strategy is only the general principle, which can be adjusted according to the different data and the understanding of some specific questions.

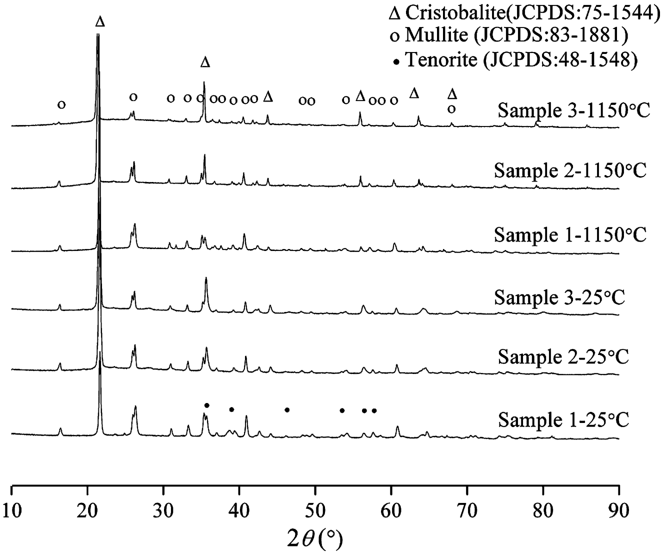

Fig. 1. XRD patterns of samples under ambient temperature and 1150 °C.

3. Results and discussion

3.1. Identification of crystalline phases and the refinement result

The comparison of the XRD pattern of high-temperature sample with that of the quenched sample in the same composition as shown in Fig. 1 reveals the presence of cristobalite and mullite solid solution whose XRD pattern was best characterized by chemical formula $Al_{4.54}Si_{1.46}O_{9.73}$ [13,14]. While, besides cristobalite and mullite, tenorite emerges in the quenched samples.

By using the crystal structures of cristobalite and mullite as the initial structure models, the Rietveld refinement of the high-temperature XRD pattern is carried out according to the refining strategy and their results are listed in Table 2.

From the results of RQA in Table 2, the relative deviations of the weight fraction of each crystalline phase is lower than 1.3% and the corresponding residual of individual refinement are steady-going and minimum enough practically. Furthermore that the variables of the high-temperature structure of phases are refined to be reasonable values prove out the reliability of the results.

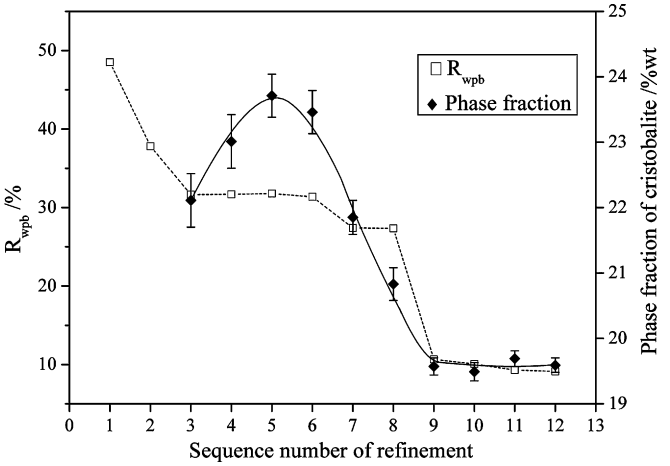

Fig. 2. Variation of residual "R_{wpb}" and phase fraction of cristobalite in the refinement process. For the meaning of sequence number of refinement, see the text.

3.2. Influences of the refined variables on the refinement results

Both the residuals and the steady accuracy of the phase fraction are the criteria to identify the quality of refinement result. In RQA of sample 1, as an example in this paper, the following variants are refined in sequence: (1) background function, (2) zero point shift, (3) phase fraction, isotropic temperature factors of (4) cristobalite and (5) mullite, lattice parameter of (6) cristobalite and (7) mullite, (8) preferred orientation of mullite, peak profile functions of (9) Ly, (10) Gv, (11) Gw and (12) Gu. The influences of these variants on the residual "R_{wpb}" and phase fraction of cristobalite are discussed below and displayed in Fig. 2.

3.2.1. Influences of background function and zero point shift

Generally, the first step of refinement is the simulation of background function with the selected background functions, which can model the amorphous scattering (the third background function in GSAS software) and model the thermal diffuse scattering at low and high diffraction angle (the sixth background function in GSAS software). It reveals that obvious difference existing in the entire pattern residuals ($R_p = \sum|I_o - I_c|/\sum I_o$, $R_{wp} = \sqrt{\sum w(I_o - I_c)^2/\sum wI_o^2}$), which are resulted from the

Table 2
The results of Rietveld refinement of the samples under 1150 °C

Sample	Crystalline phase	Weight percent (%)	Lattice parameter		Temperature factor (Å^2)	R_{wpb} (%)	R_{pb} (%)
			a, b, c (Å)	v (Å^3)			
1	Cristobalite	19.6 (1)	7.14867 (5)	365.32 (8)	0.0305 (8)	9.12	5.80
	Mullite	80.4 (1)	7.5502 (5), 7.7410 (6), 2.8979 (2)	169.37 (2)	0.0112 (8)		
2	Cristobalite	57.5 (1)	7.1481 (3)	365.23 (5)	0.073 (1)	7.13	5.11
	Mullite	42.5 (2)	7.5727 (5), 7.7438 (5), 2.9017 (2)	170.16 (2)	0.023 (1)		
3	Cristobalite	75.3 (10)	7.1509 (7)	365.7 (1)	0.033 (1)/0.096 (2)[a]	10.74	6.55
	Mullite	24.7 (3)	7.563 (4), 7.740 (4), 2.897 (1)	169.6 (2)	0.0002 (1)		

[a] Isotropic temperature factors of the atoms of Si and O in cristobalite: Si/O.

Table 3
Residuals' comparison from different background functions in the background fitting

Number of polynomial term	The third background function		The sixth background function	
	R_{wp} (%)	R_p (%)	R_{wp} (%)	R_p (%)
2	20.57	14.61	20.05	14.49
3	20.57	14.61	19.01	13.60
4	99.99	99.99	16.81	10.45
6			16.18	9.79
8			16.01	9.80
10			15.65	9.35
12			Divergence	

different background functions and the number of polynomial terms (Table 3). The sixth background function with 10 terms gives the lowest entire pattern residuals, which indicates that the influence of thermal diffuse scattering in high temperature is larger than that of amorphous scattering.

Secondly, system deviation from zero point shift has to be refined because the sample's thickness is inevitably changed during the high-temperature data collecting process. For example, about −0.01216° (2θ) of the zero point shift of sample 1 refined the calculated reflection intensity (I_c) through formula (5) and consequently decrease the residuals (R_{wpb} and R_{pb}) from 48.53 and 26.27 to 37.82 and 22.18, respectively (Fig. 2).

3.2.2. *Refinement of the reflection intensity of crystalline phases*

The refinement of phase fraction is a beginning of refining the reflection intensity of crystalline phases. The convergence of the refinement, the reducing of phase fraction of cristobalite to 22% as well as the remarkable decreasing of residual R_{wpb} to 30% proves the validity of the refining strategy until now. Evermore, the validity of refinement can be monitored with both phase fraction of cristobalite and the residual R_{wpb} as demonstrated in Fig. 2.

The Bragg reflection intensity of the *p*th phase (Y_p) as displayed in formula (5) is contributed from structure factor (F_p), the peak profile shape function at any diffraction angle ($H(T-T_p)$) and the correction factor (K_p) of the *p*th phase:

$$Y_p = F_p^2 H(T - T_p) K_p \qquad (5)$$

Primarily, there are more effects of high temperature on temperature factors of atoms and lattice parameters of unit cell, which are related with structure factor (F_p) and peak profile shape function ($H(T-T_p)$), respectively. Practically, the refinement will be divergence when temperature factors and lattice parameters are not refined ahead. Converge was achieved when the isotropic temperature factors of cristobalite and mullite following the lattice parameters of cristobalite were refined although the phase fraction of cristobalite gradually increases with more than 5% average deviation on the basis of the Bragg diffraction residual (R_{wpb})*** keeping invariant as shown in Fig. 2. The origin is from the refinement of the deficient structure variables. Further setting active of the lattice parameters of mullite brings obvious decrease in the residual, which attributes to the fact that the coefficient of thermal expansion of mullite is larger than that of cristobalite (the volume of mullite increases by 1.1% and that of cristobalite by 0.77%). Resultantly, the enlargement of the lattice parameters of mullite has more effects on the reflection intensity (Y_p) as well as to reduce the residuals of refinement in high-temperature RQA.

Although there is no too much falling down in the residuals caused by the refinement of preferred orientation of mullite, the phase fraction of cristobalite diminishes with evidently reduced average deviation. This indicates that the crystal structure becomes more reasonable after the main structure factors have been refined. So fitting the profile parameters of pseudo-Voigt II profile function in time will get residuals small enough and more stable. Finally, the phase fraction reaches accuracy of *ca.* 1% accompanying with the residuals lower than 10%.

According to the above analysis on the high-temperature RQA refinement, the primary consideration is the simulation of the effect of background scattering on the XRD pattern if the sample consists of amorphous and crystalline phases. And the thermal diffuse scattering polynomial is much more suitable for the refinement of high-temperature background. Sequentially, the temperature factors and lattice parameters of crystal structure should be refined at first because both the parameters have large changes at high temperature. This is the prerequisite for the refinement of the other structure factors even if the residuals decrease slightly in the refinement. Preferred orientation is the most important factor in the QXRPD method for anisotropic crystalline phases while RQA method can effectively reduce the contribution of preferred orientation to the quantitative analysis. After all of the above parameters have been refined, the parameters of peak profile shape functions are refined at last. Consequently, the anticipant QXRPD accuracy such as 1% accuracy of phase fraction will be obtained on the basis of the correct crystal structure when the residual is lower than 10%. It is obvious that the lower the residual is, the more the accurate phase fraction will reach.

3.3. *Accuracy of the refinement results and its application in the phase diagram*

According to the phase equilibrium and phase boundary rule [15,16], when the ternary system reaches the solid–liquid equilibrium in a three-phase tie-plane at a specific temperature, the solid phase points of all compositions in the tie-plane balances with the unique liquid phase point which is a corner of the tie-plane, namely the tie-lines of all compositions in the tie-plane intersect on a corner of the tie-plane. According to the preliminary analysis result of the isothermal phase diagram of Cu_2O–Al_2O_3–SiO_2 pseudo-ternary system at 1150 °C, the three compositions of samples 1–3 in this work locate in tie-plane of cristobalite, mullite and liquid phase. Accordingly, the three tie-lines of these compositions will encounter on the corner of the tie-plane.

As shown in Fig. 3 three tie-lines meet on the corner of the tie-plane in the determination deviation by extending the beeline from solid phase point, which is determined from RQA method, to the composition point of the system. The values of the cross-

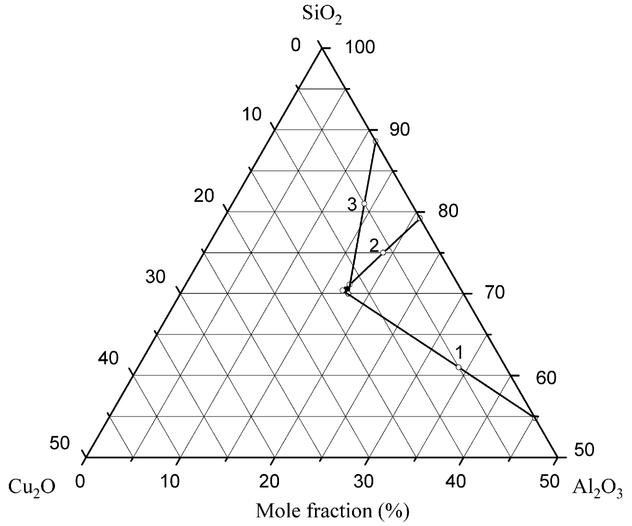

Fig. 3. The compositions of the samples and crystal phase ratios of each sample resulting from *in situ* high-temperature RQA. Crosspoint of the tie-lines confirms the reliability of RQA method.

Table 4
Compositions of the solid phase points and the crosspoints of the tie-lines of the three system compositions (mol%)

Sample	Solid phase point		Sample	Crosspoint of the tie-line		
	Al_2O_3	SiO_2		Cu_2O	Al_2O_3	SiO_2
1	45.2	54.8	1–2	12.6	17.0	70.4
2	20.8	79.2	1–3	12.2	17.8	70.0
3	11.4	88.6	2–3	11.5	17.4	71.1
Average				12.1 ± 6	17.4 ± 4	70.5 ± 6

points and the deviations are listed in Table 4. Therefore, the composition of the molten liquid phase in the tie-plane can be determined by high-temperature RQA standardless method even though the quantitative analysis of this liquid phase cannot be directly carried out by RQA method.

By comparison, it reveals that the deduced relative errors (about 5.0%) of Cu_2O are bigger than that of compositions of SiO_2 and Al_2O_3 which is directly determined (0.1–2.3%) and principally resulted from the error accumulation. Therefore, it is reliable for the *in situ* high-temperature RQA standardless method applied in this paper. The degrees of accuracy and precision can be obtained by selecting different refining strategies according to the requirements.

4. Conclusion

A method has been described to extend the application of the RQA standardless method to *in situ* high-temperature QXRPD of Cu_2O–Al_2O_3–SiO_2 pseudo-ternary system. By using the qualitative analysis result of three quenched samples as the initial structure model, the RQA of their *in situ* high-temperature XRD data have been carried out according to the designed refining strategy. The precision has been proved and the results can be applied in the determination of the three-phase region of the isothermal phase diagram of Cu_2O–Al_2O_3–SiO_2 pseudo-ternary system.

The influences of some variables on the refinement have been analyzed including that high-temperature scattering function can give a satisfaction fit for the background refinement, and it is necessary to fit zero point of the diffraction pattern, temperature factors of atoms and lattice parameters of unit cells because they withstand large changes at high temperature. The influence of preferred orientation to the quantitative analysis can be effectively reduced in RQA standardless method. The precisions and accuracy of phase fraction can be achieved according to the anticipation and it is obvious that the lower the residual is, the more accurate phase fraction will reach.

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