

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 $\text{Cu}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ 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%.

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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 $\text{Cu}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ 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 Cu₂O–Al₂O₃–SiO₂ samples (mol%)

Sample	SiO ₂	Al ₂ O ₃	Cu ₂ O
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 Cu₂O–Al₂O₃–SiO₂ 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 Cu₂O–Al₂O₃–SiO₂ 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 HNO₃ 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 12h, 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 Cu₂O 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 X³-Pert MPD diffractometer with X³Celerator detector using Cu K α 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° (2 θ) with a step size of 0.0167° (2 θ) 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 p th 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 $R_{w_p}/R_{w_{pb}}$ 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.

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