Quantitative Determination of the Crystalline Phases of the Ceramic Materials Utilizing the Rietveld Method

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Abstract

Ceramic materials have properties defined by their chemical and micro-structural composition. The quantification of the crystalline phases is a fundamental stage in the determination of the structure, properties and applications of a ceramic material. Within this context, this study aims is the quantitative determination of the crystalline phases of the ceramic materials developed with addition of mineral coal bottom ash, utilizing the X ray diffraction technique, through the method proposed by Rietveld. For the formulation of the ceramic mixtures a {3,3} simplex-lattice design was used, giving ten formulations of three components (two different types of clays and coal bottom ash). The crystalline phases identified in the ceramic materials after sintering at 1150^{o}C during two hours are: quartz, tridimite, mullite and hematite. The proposed methodology utilizing the Rietveld method for the quantification relating to crystalline phases of the materials was shown to be adequate and efficient.

Introduction

The quantification of the crystalline phases is a fundamental stage in the determination of the structure, properties and applications of a ceramic material. Rietveld [1] developed a method to refine structures, based on the comparison between a calculated diffraction pattern and the observed one, which has been extended after to be applied in the quantitative phases analysis and micro-deformation studies. The Rietveld Method considers crystallographic theoretical data (crystalline system, spatial group, atomic positions, system parameters, occupation number and isotropic temperature factor) of crystalline phases.

The Rietveld Method is based on the comparison between a diffraction pattern and the observed pattern. The calculated pattern is obtained using the single cell as a basis. This calculated pattern is, so, compared to the observed pattern and the model parameters are adjusted by the minimum square method [2]. The Rietveld Method presents difficulties in quantitative determination of the fraction of the material amorphous part. This way, quantitative percentage of crystalline phases, determined by Rietveld Method, are relative, not considering the amorphous

phase. In this case, it is necessary the crystalline determination (or % of amorphous phase) through another method.

The Rietveld Method allows, simultaneously, to refine the single cell and the crystalline structure, micro-structure and quantitative phases analysis and determination of preferred orientation [3].

Statistical numerical indicatives, R_P e $R_{WP,}$ are comparative parameters between theoretical and experimental X ray patterns. These can be used to follow the model convergence. R_P e R_{WP} must reach the R_{EXP} value in order to the modeling be acceptable. Equations 1, 2 e 3 define indicators R_P, R_{WP} e R_{EXP} respectively:

$$R_P = 100\left\{\frac{\left[\sum I_{iO} - I_{iC}\right]}{\sum I_{iO}}\right\}, \quad (1)$$

$$R_{WP} = 100\left\{\frac{\left[\sum x(I_{iO} - I_{iC})^2\right]}{\sum x_i (I_{iO})^2}\right\}^{\frac{1}{2}}, \quad (2)$$

$$R_{EXP} = 100\left\{\frac{(N-P)}{\left[\sum x_i (I_{iO})^2\right]}\right\}^{\frac{1}{2}}. \quad (3)$$

Where: I_{i0} is the observed intensity in angular position i; I_{iC} is the calculated intensity in angular position i; N is the number of experimental points; P is the number of refined parameters; R_B is the convergence factor based on experimental spectrum intensities; R_{XB} is the convergence factor based on experimental spectrum intensities and on found concentrations and e R_{exp} is the factor related to the spectrum experimental quality.

Within this context, this study aim is the quantitative determination of the crystalline phases of multiphase systems through the method proposed by Rietveld. Studied samples are ceramic materials developed with addition of mineral coal bottom ash as raw materials.

Materials and Methods:

Material characterized in this study are ceramic materials for covering with addition of mineral coal bottom ash, sinterized at 1150 ^oC to 2 hours.

X Ray diffraction analysis of the developed material were obtained with a Philips X´Pert equipment, (λ = 1,54 Å) through the powder method. Analyses were done with 0,02^o/ 2s and 2θ from 10 to 90^o.

Crystalline phases were identified based on JCPDS database [4].

In order to obtain the crystallographic data, necessary to the structural refinement through the Rietveld Method, it was used the ICSD [5]. Input data to the refinement by the Rietveld Method are presented in Table 1.

The used refinement program was the DBWS 98. DMPLOT program made possible the comparison between the theoretical spectrum and the refined one.

Table 1. Crystallographic theoretical data of crystalline phase present in sinterized ceramic materials.

Phase	Lattice parameters (Å)	Atomic Position	Occupation Number	Thermal Isotropic Factors (B_o)
Quartz (α-SiO_2) ICSD 29210 PDF 05-490 P 32 2 1 S (154)	a = b = 4,913 c = 5,405 $\alpha = \beta = 90$ $\gamma = 120$	Si (3a), x = 0,469, y = 0,0, z = 0,0 O (6c), x = 0,403, y = 0,253, z = 0,122	Si = 1,0 O = 1,0	B_o (Si) = 0 B_o (O) = 0
SiO_2 ICSD 34889 PDF 76-0912 P 43 21 2 (96)	a = b = 7,456 c = 8,604 $\alpha = \beta = \gamma = 90$	Si (8b), x = 0,326, y = 0,120, z = 0,248 Si (4a), x = 0,410, y = 0,410, z = 0,0 O (8b), x = 0,445, y = 0,132, z = 0,400 O (8b), x = 0,117, y = 0,123, z = 0,296 O (8b), x = 0,334, y = 0,297, z = 0,143	Si (8b) = 1,0 Si (4a) = 1,0 O (8b) = 1,0 O (8b) = 1,0 O (8b) = 1,0	Si (8b) = 2,39 Si (4a) = 2,39 O (8b) = 2,39 O (8b) = 2,39 O (8b) = 2,39
Tridimita (SiO_2) ICSD 29343 PDF 75-0638 P 63 2 2 (182)	a = b = 5,01 c = 8,18 $\alpha = \beta = 90$ $\gamma = 120$	Si (4f), x = 0,333, y = 0,667, z = 0,47 O (2c), x = 0,333, y = 0,667, z = 0,25 O (6g), x = 0,425, y = 0,0, z = 0,0	Si (4f) = 1,0 O (2c) = 1,0 O (6g) = 1,0	B_o (Si) = 0 B_o (O) = 0
Mulita ($Al_{2,35}Si_{0,64}O_{4,82}$) ICSD 23726 PDF 15-776 P B A M (55)	a = 7,566 b = 7,682 c = 2,884 $\alpha = \beta = \gamma = 90$	Al (2a), x = y = z = 0,0 Al (4h), x = 0,2380, y =0,2945, z = 1/2 Al (4h), x = 0,3512, y = 0,1590,z = 1/2 Si (4h), x =0,3512, y = 0,1590, z = 1/2 O (4g), x =0,3729, y = 0,2808, z = 0,0 O (4h), x = 0,1420, y = 0,0777, z = 1/2 O (2d), x =0,0, y = 1/2, z = 1/2 O (4h), x = 0,0509, y = 0,4482, z = ½	Al (2a) = 1,0 Al (4h) = 0,34 Al (4h) = 0,34 Si (4h) = 0,33 O (4g) = 1,0 O (4h) = 1,0 O (2d) = 0,41 O (4h) = 0,21	Al (2a) = 0,43 Al (4h) = 0,51 Al (4h) = 0,49 Si (4h) = 0,49 O (4g) = 0,97 O (4h) = 0,92 O (2d) = 1,4 O (4h) = 0,84
Hematita (Fe_2O_3) ICSD 15840 PDF 13-0534 R -3 C H (167)	a = b = 5,038 c = 13,772 $\alpha = \beta = 90$ $\gamma = 120$	Fe (12c), x = 0,0, y = 0,0, z = 0,3553 O (18e), x = 0,3059, y = 0,0, z = 0,25	Fe = 1,0 O = 1,0	B_o (Fe) = 0 B_o (O) = 0

Results and Discussion

Crystalline phases identification. Figure number 1 presents the X ray patterns of ceramic material studied: MA, MB, MC, MD. These materials were obtained in the paper described by KNIESS [6]. Identified crystalline phases (in ceramic materials) are also presented in Figure 1.

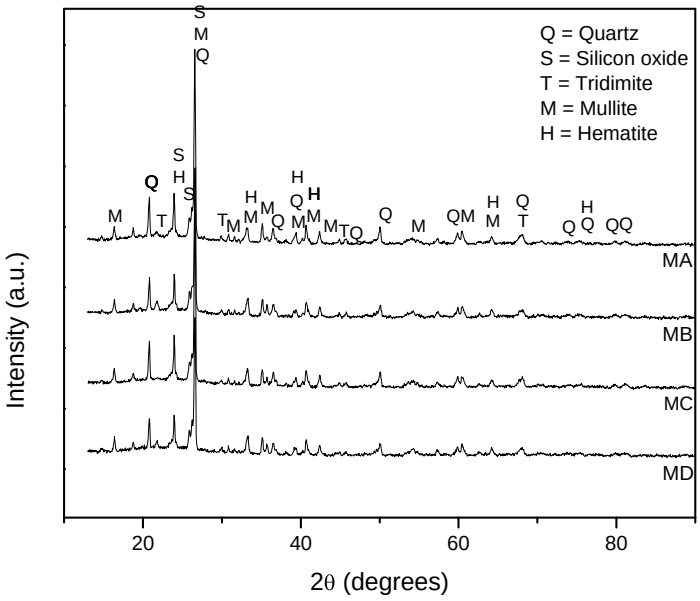

Figure 1. X Ray patterns of ceramic materials, sinterized under the temperature of 1150^0C.

Crystalline phase quantification by Rietveld.

Figure 2 presents the comparison between the experimental pattern and MA, MB, MC and MD samples simulation, through the Rietveld Method. Materials MA, MB, MC and MD spectrum plotting presented a good approach to the diffraction pattern simulated and the observed one, with a good definition to intensities and peak positions.

Percentage related to crystalline phases, obtained through the Rietveld Method, is presented in Table 2, which also presents statistical numeric indicators R_P, R_{WP} e R_{EXP}.

Crystalline and amorphous phases characteristics are considered very important factors, which influence mechanical properties of ceramic materials [7]. Quartz and mullite were identified as major crystalline components in all eleven samples. It is possible to observe that the MA material presented the highest percentage of residual quartz after sintering (54,89%). MC material present the highest percentage of tridymites phase in comparison with the other materials obtained (8,39%). MD material presented the highest percentage of mullite phase (22,45%) and hematite phase (14,49%).

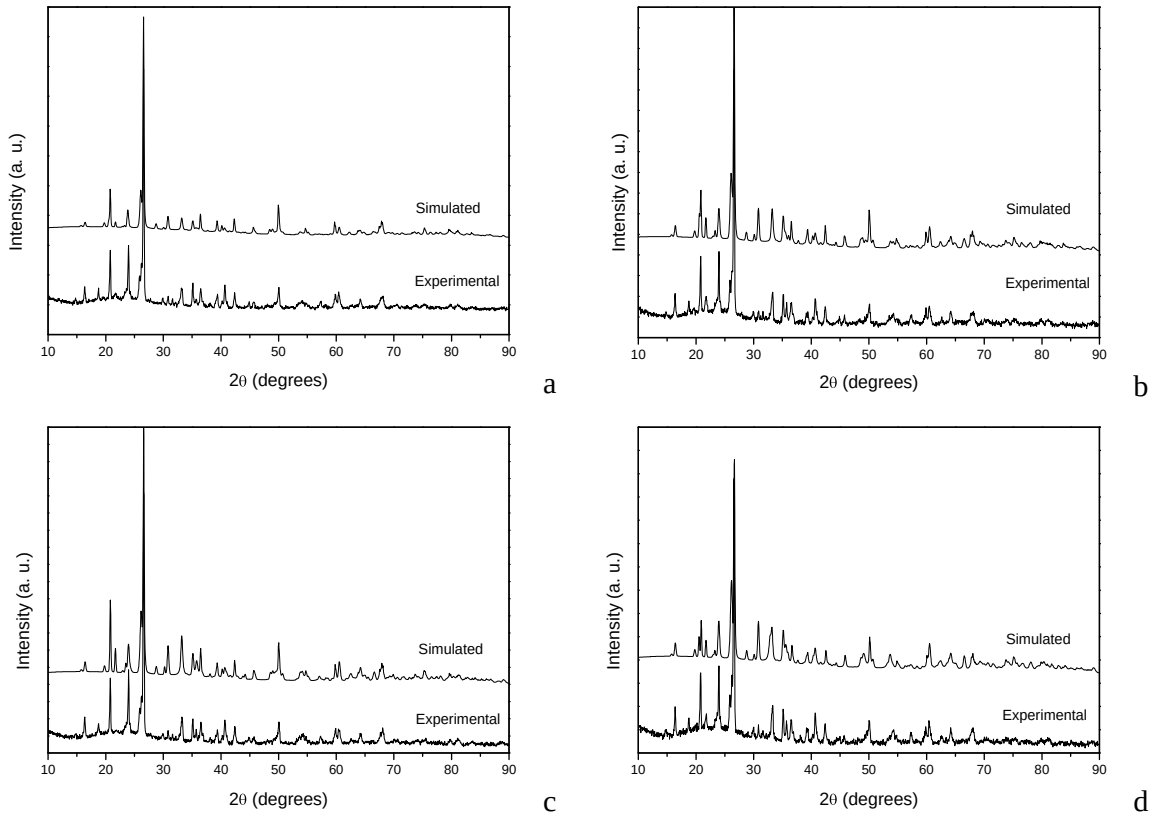

Figure 2. Materials MA, MB, MC and MD patterns, experimental and simulated by the Rietveld Method.

Table 2. Statistical numeric indicators R_P, R_{WP} e R_{EXP} and related percentage calculated through Rietveld of crystalline phases.

Sample	R_P* (%)	R_{W-P}* (%)	R_{EXP}* (%)	Relative percentage of the crystalline phases calculated by Rietveld Method				
				α -Quartz	Silicon oxide	Tridimite	Mullite	Hematite
MA	7,41	9,97	3,32	54,89	21,32	3,31	15,91	4,58
MB	7,27	10,23	3,19	39,90	19,92	7,20	23,25	9,73
MC	8,92	12,39	3,22	37,76	18,66	8,39	19,95	15,24
MD	8,66	13,0	3,18	29,11	21,11	6,05	26,56	17,14

The structural refinement of MA material presented the lowest of R_{W-P} (9,97%). Convergence was verified through indexes R_P e R_{W-P}. In despite of the fact that R_P e R_{W-P} are distant more that the 20% recommended, experimental and simulates spectrum curves presented a good correspondence (Figure 2a), and the R_{W-P} value is within the recommended range for good results ($2 \leq R_{W-P} \geq 10$).

Pattern of MB material presented a good approaching between the simulated diffraction pattern and the observed one, with a good definition to the intensities and peak positions, as shown in Figure 2b. Refinement quality indicators are R_P =7,27 %, R_{WP} = 10,23 % and R_{EXP} =3,19 %.

It is possible to observe that, to MC material, there is also a higher difference between peaks intensities than in the pattern, experimental and simulated in the lower angles region, where more intense peaks are placed (Figure 2c). Refinement quality was evaluated through R_P e R_{W-P} indexes, equals to 8,92% and 12,39 %, respectively, while R_{EXP} was 3,22%. In despite of the difference between entre R_{W-P} and R_{EXP} is higher than the recommended 20%, simulated and experimental spectrum curves present good concordance, and the R_{W-P} value is within the recommended range in literature [8].

Crystalline phases structural refinement of MD material was the one which presented the highest R_{W-P} value (13,0%) compared with the structural refinement done in the other materials. Convergence Indexes R_P e R_{EXP} were equals to 8,66%, and 3,18% respectively.

Conclusions

The Rietveld Method showed itself to be a worth tool for structural and quantitative analysis of phases. Refinement through Rietveld Method showed itself as a high reproducibility technique with advantages concerning technical and logistic point of view. The possibility of quantifying crystalline phases of multiphasic material, as well as obtension of quantitative results of crystalline phases between poly morphs from a same phase, are characteristics which justified the use of DRX – Rietveld Method.

Quantitative percentage of crystalline phases was determined in terms of relative percentage, that is, without considering the fraction of amorph part. The Ruland method [9] is an alternative to determine the crystallinity of this materials.

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