

EFFECTS OF CRYSTALS PREFERENTIAL ORIENTATION ON PHASES QUANTITATIVE ANALYSIS BY **RIETVELD METHOD**

matériaux

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Context

Rietveld method applied to XRD patterns is widely used for phase structure refinement or quantitative analysis. The calculated intensity I_i^{calc} at step i of the simulated pattern is given by the general equation:

$$I_{i}^{calc} = S_{F} \sum_{j=1}^{Nphases} S_{j} \sum_{k=1}^{Npeaks} I_{k,j,i}P_{k,j}A_{j,i}L_{i} + bkg_{i}$$

Preferential orientation factor

The anisotropic distribution of the lattice planes k with regards to the analyzed surface for a given phase j can be taken into account throughout the factor $P_{k,j}$. For a cylindrical texture symmetry in a Bragg-Brentano diffractometer geometry, $P_{k,j}$ is given by the March-Dollase equation

With $I_{k,j,i} = m_{k,j} |F_{k,j}|^2 G_j (2\theta_i - 2\theta_{k,j})$ and $S_j = f_j V_j^2$

Quantitative analysis of weight fraction f_j is based upon the scale intensity factor S_j for each phase j. Problem: preferential orientation of crystals modifies relative intensities $I_{k,j,i}$ of the diffraction peaks, what may affect S_j and consequently the calculated weight fractions.

<u>Our work</u>

- To prepare and analyze mixtures of rounded shaped SiO₂-quartz particles (q) with rounded or platelet shaped α -Al₂O₃ particles (a).
- To check the influence of preferential orientation of the (00l) lattice planes for platelets on the quantitative analysis (MAUD Rietveld software).







Platelets shaped α-Al₂O₃ particles (SEM micrograph)

Rounded shaped α-Al₂O₃ particles (SEM micrograph)

Rounded shaped SiO₂-quartz particles (SEM micrograph)

Two configurations investigated for the specimen conditioning prior to XRD

 α is the angle between the normal \vec{n}_K to the lattice planes K that are preferentially oriented parallel to the analyzed surface and the normal \vec{n}_k to the diffracting lattice planes k. G_K , is the refinable parameter that quantifies the preferential orientation of lattice planes K.

 $P_{k,j} = \frac{1}{m_{k,j}} \sum_{1}^{m_{k,j}} \left(G_{K,j}^2 \cos^2 \alpha_{K,k,j} + \frac{1}{G_{K,j}} \sin^2 \alpha_{K,k,j} \right)^{-1}$





Rietveld refinement of Platelets shaped α -Al₂O₃ free powder: a) without b) with taking into account preferential orientation through refinement of G_k coefficient

analysis: I)- free powder in the holder; ii)- 100 MPa pressed pellets.

Test #	Phases	Al ₂ O ₃ particles	Specimen	
(weight fractions)		morphology	conditioning	
1	Al₂O₃ (100)	Rounded	Free	
2	Al₂O₃ (100)		Pressed	
3	Al₂O₃ (100)	Platelets	Free	
4	Al₂O₃ (100)		Pressed	
5	SiO ₂ (100)	Rounded	Free	
6	Al ₂ O ₃ /SiO ₂ (50/50)	Rounded	Free	
7	Al ₂ O ₃ /SiO ₂ (50/50)	Platelets	Free	
8	Al ₂ O ₃ /SiO ₂ (50/50)	Platelets	Pressed	

Phases Data

	Al ₂ O ₃		
Symmetry	Trigonal		
Space group	R-3c : H		
Cell parameters	a = 4.760		
	b = 12.993		
Structure	Al	0	
Total occupancy	1	1	
Biso factor	0	0	
Total quantity	12	18	
	X = 0	X = 0.31	
Position	Y = 0 Z = 0.35	Y = 0 Z = 0.25	

SiO ₂						
Symmetry	Trigonal					
Space group	P3221					
Cell parameters	a = 4.916					
	b = 5.4054					
Structure	Si	0				
Total occupancy	1	1				
Biso factor	0	0				
Total quantity	3	6				
	X =0.47	X = 0.41				
Position	Y = 0 Z = 0.67	Y = 0.27 Z = 0.78				

Test #	R _{exp}	R _{wp}	S	G a(006)	P _{a(006)} (%)	f _a	fq
1	15.1	18.3	1.21	0.886	20	100	-
2	16.5	20.8	1.26	0.865	24	100	-
3	15.4	20.5	1.33	0.536	155	100	-
		34.4	2.23	1	1	100	-
4	17.4	22.2	1.27	0.555	142	100	-
5	12.8	19.9	1.55	1	1	-	100
6	15.6	21.5	1.38	1	1	53.4	46.6
7	15.1	25.8	1.71	1	1	48.1	51.9
		21.0	1.39	0.588	122	51.2	48.8
	23.8	37.1	1.56	1	1	48.7	51.3
8		31.7	1.33	0.560	137	53.3	46.7



R_{wp}: weighted profile R-factor

R_{exp}: expected R-factor

S = $\frac{R_{wp}}{R_{exp}}$: Goodness of Fit

- Rounded shaped α-Al₂O₃ particles are not significantly oriented in the holder while platelets are strongly oriented
- Specimen conditioning (free or pressed configuration) doesn't strongly affect the preferential orientation phenomena
- The presence of rounded shaped SiO₂-quartz particles_, slightly decreases the orientation of α -Al₂O₃ particles in the sample
- A difference of about 6-8 % in the calculated weight fractions is observed when preferential orientations are not taken into account



A correct phases quantitative analysis of non-rounded particles by the Rieltveld method requires to take into account phenomena of preferential orientations. In addition, taking into account microabsorptions of different phases allowed to correct deviations of calculated weight fractions from their real value.

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