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X-RAY DIFFRACTION PHASE ANALYSES FOR GRANULATED AND SINTERED CERAMIC MATERIALS

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Abstract

One basic problematic aspect in x-ray diffraction phase analysis is microabsorption effect which may arise from the size of the crystallite phases. Complication of the problem may intensify in sintered ceramic materials where milling of the samples is not simple. We report the Rietveld x-ray diffraction phase analysis of MgO-α-Al_2O_3 powder mixtures with phase content ratio of 1:1 by weight and MgO-Y_2O_3 sintered ceramic composites with Y_2O_3 contents of 10%, 20% and 30% by weight. The mixtures were pre-sintered at 1000°C for 2 hours and then milled while the composites were sintered at 1550°C for 3 hours. The phase composition analysis was done using *Rietica*, a non-commercial Rietveld method-based software. Relative and absolute phase compositions were examined and results showed that there was a significant amount of phase composition bias resulted from the examination. For the powder mixture, milling can reduce microabsorption effect and hence the calculation bias. For the ceramic composite where milling is almost impossible, additional of Y_2O_3 caused smaller crystallite size of MgO, so that composition bias is smaller in composites with higher Y_2O_3 content. A mathematical model is proposed to provide more acceptable phase composition results.

Keywords: Rietveld phase analysis, MgO-Y_2O_3 composites, sintered ceramics

1. Introduction

Possibly the most popular tool for phase composition of materials using powder diffraction data is Rietveld method (1969) [1] as it particularly is able to deal with overlapping peaks (Hill, 1993) [2]. The method has been applied to various materials such as oxide powders (for example Hill and Howard, 1987; Purnadewi 2004) [3,4] and sintered ceramics (for example Pratapa, 1997 and 2003) [5,6]. Basic step known for anticipating the effect of large grain powder is by mechanical milling. Large grains, together with absorption, would reduce diffracted intensity which may result in bias in phase composition calculation. Moreover, there is a complication of obtaining fine powders if the tested materials is in the form of sintered ceramic. The problem would take a more serious difficulty if the materials consist of hard phases.

A systematic study in order to identify the existence of bias in phase composition analysis using Rietveld method has been performed using two systems. The first used mixture of MgO and α-Al_2O_3 powders, while the second used MgO and Y_2O_3 compacted ceramics. They also exhibit pronounced absorption contrast effect shown by their absorption coefficient, ie. 26.8 cm^{-1} (MgO), 131.7 cm^{-1} (Al_2O_3) and 102.5 cm^{-1} (Y_2O_3) for

Cu Kα (Cullity, 1978) [7]. We report the analysis of x-diffraction data of the powder mixtures, sintered ceramics and also a simple, empirical model for correcting the bias in the composition calculation.

Theoretical Background. Assuming that a mixture contains no amorphous phase (totally crystalline), the relationship between Rietveld phase scale and relative phase weight fraction is in the form of (Hill and Howard, 1987) [3]

(1)

where w_i is relative weight fraction of phase i (%), s is Rietveld phase scale, Z is number of formula in unit cell, M is formula weight and V is volume of unit cell. To accommodate absorption effect, Eq. (1) is modified into (Bish and Howard, 1988) [8]

(2)

where w_s is the weight fraction of the internal standard and μ_{sample} is the absorption coefficient for the designated mixture. Taylor and Matulis (1991) [9] argued that the weight fraction expression should take into account the absorption characters of each phase so that Eq. (1) becomes

(3)

where τ_i is a particle absorption factor for phase i and taking a form of

(4)

where A_i is the volume of particle of phase i and is the mean linear absorption of the solid mixture. They concluded that quantitative Rietveld phase analysis should include corrections for Brindley particle absorption contrast effect which is also known as microabsorption effect. Inaccurate results were obtained if absorption contrast is present in the mixture. The calculation is performed after use of SEM to acquire the particle size estimate. The last step is practically tedious since two instruments are required to complete one calculation. Meanwhile, it is known that crystallite size (which maybe equivalent to particle size to some extent) can be extracted from Rietveld analysis through (Pratapa et. al., 2002) [10]

(5)

where D is crystallite size, λ is the radiation wavelength, H_L is the refinable Lorentzian component peak breadth of a phase and H_{LS} is the Lorentzian component peak breadth of a standard material representing the breadth effect of the instrument.

2. Research Method

MgO-α-Al_2O_3 powder mixtures were made by weight ratio of 1:1. MgO powder was calcined at 700 °C for 1 hour prior to mixing to remove absorbed water vapor. To introduce large grain effect, one of the powder was presintered at 1000 °C for 1 hour. Milling was performed using a conventional rotating milling to reduce back the large grains. Identification for the powders showed that there were only two phases in the

	Milling time (hours)			
	0	1	2	3
Periclase *as-received* + corundum *as-received*	PAKAO	-	-	-
Periclase presintered + Corundum *as-received*	PPKAO	PPKA1	PPKA2	PPKA3
Periclase *as-received* + corundum presintered	PAKPO	PAKP1	PAKP2	PAKP3

mixtures, ie. periclase (MgO) and corundum (α-Al_2O_3). Numenclature for the samples are given as follows.

Mixtures of MgO-Y_2O_3 with compositions of 90-10, 80-20 and 70-30 by weight were made by conventional milling. Each mixture was then uniaxially pressed at 37 MPa to obtain green body prior to sintering at 1550°C for 3 hours. The sintering produced ceramic composites with more than 95% density.

Diffraction data were collected using a diffractometer with Cu target at 40 kV and 30 mA with 2θ range of 10-120°, 0.02° step size and 1 s collecting time per step. Rietveld analyses were performed using *Rietica* (Hunter, 1998) [11].

3. Results and Discussion

Figures 1 show the x-ray diffraction (XRD) patterns for the MgO-α-Al_2O_3 powder mixtures (left) and MgO-Y_2O_3 ceramic sintered composites (right). The diffraction patterns for the MgO-α-Al_2O_3 powder mixtures with variation of presintering conditions show no significant difference. On the other hand, it is obvious that the intensities of phases in the MgO-Y_2O_3 ceramic sintered composites change systematically with composition as expected. In general, intensity for MgO decreases with reduced MgO content whereas that for Y_2O_3 increases with increased Y_2O_3 content.

Rietveld analysis performed to the collected XRD patterns was successful indicated by key figures-of-merit (FoMs) which are, for the ceramic composites, tabulated in Table 1. According to Kisi (1994) [12], all FoMs are acceptable since goodness-of-fit (GoF) is less than 4% and R_{wp} is less than 20% for the XRD patterns. Visual inspection to the fitting plots also indicates the accomplishment of the Rietveld refinement. Example of the final fitting plot for the MgO-Y_2O_3 ceramic composites with 90-10 composition is shown in Figure 2. As can be seen, difference plot between calculated and observed patterns shows minor fluctuation. These observations infer that the output of the refinement can be used to perform further analysis such phase composition and crystallite size calculations.

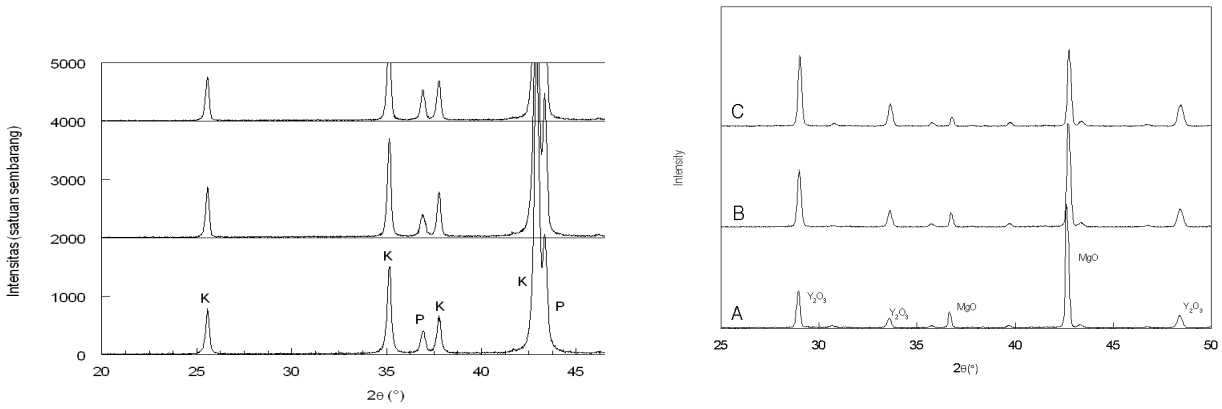

Figure 1. XRD patterns for (left) MgO-α-Al_2O_3 powder mixtures [PAKA0 = without heat treatment, PAKP0 = after presintering of α-Al_2O_3 and PPKP0 = after presintering MgO] and (right) MgO-Y_2O_3 ceramic composites with 90-10 (A), 80-20 (B) and 70-30 (C) weight compositions. Radiation used was CuKα (λ = 1.5418 Å – weighted).

Table 1. Rietveld refinement output of the whole-pattern diffraction data for MgO-Y_2O_3 ceramic composites

Sample (MgO-Y_2O_3)	Figures-of-merit				Scale factor		H_L	
	R_p	R_{wp}	R_{exp}	GoF	MgO	Y_2O_3	MgO	Y_2O_3
90-10	9.58	12.62	9.89	1.62	0.009333	0.00000324	0.03377	0.03944
80-20	8.55	11.15	9.12	1.49	0.008337	0.00000501	0.04375	0.03453
70-30	8.24	11.19	8.93	1.57	0.006202	0.00000614	0.04415	0.0342

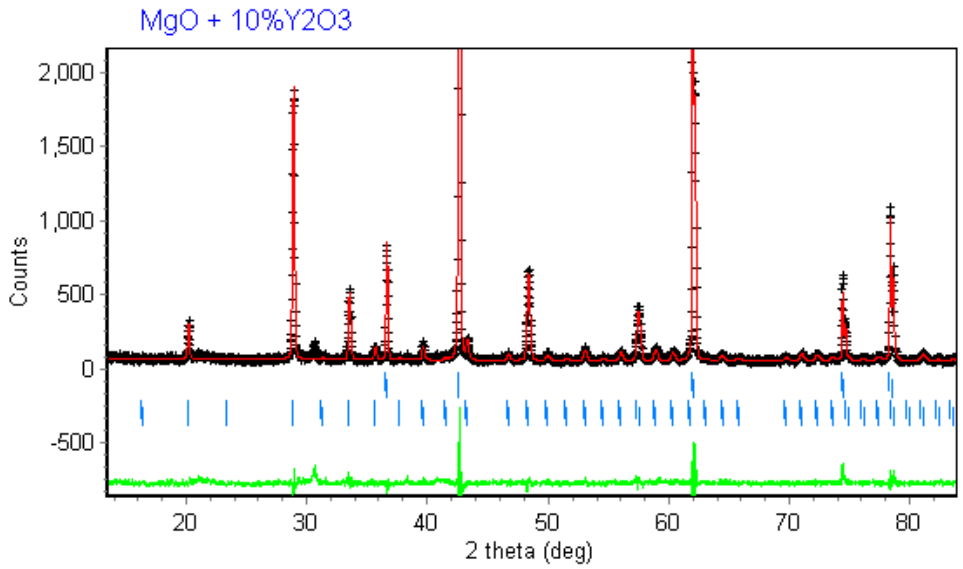

Figure 2. Rietveld refinement plot for an MgO-Y_2O_3 ceramic composite with 90-10 weight composition. The observed data are represented by a (+) sign and the calculated data by a solid line. Vertical lines represent the positions of diffraction lines of MgO and Y_2O_3, respectively. The line below the plot is the difference profile.

Table 2 shows the absolute weight fractions of phases in the MgO-α-Al_2O_3 powder mixtures. Either MgO or α-Al_2O_3 was used as standard, where its content was then constrained to 50%. In general, it can be inferred that (1) the composition of the non-pre-sintered mixture was 1:1 by weight as expected, (2) pre-sintering has indirectly caused bias on the phase composition calculation, and (3) milling can reduce such bias. The results can be explained as follows. The original powders had insignificant absorption contrast and their initial crystallite sizes are sufficiently small so that microabsorption effect was not observed. As a result, the phase composition calculation gave accurate results. When a powder was presintered, its crystallite size started to grow. According to theory of intensity reduction due to absorption (see, for example, Cullity, 1978) [7] where μ is absorption coefficient and x is one-dimensional geometric quantity, when x-ray passes through a thick homogeneous material, its intensity reduces more significantly. Reduction of intensity causes reduction of phase scale in Rietveld refinement. As a result, using Eq. (2), its content may deviate, as shown in Table 2. However, when the powders were milled, their crystallite size reduces back, resulting in the accurate composition calculation. This systematic study gives two significances, ie. (1) microabsorption effect can be caused by large crystallite size and (2) milling can be used to reduce the effect. However, there are two problems which may arise in routine x-ray diffraction analysis, ie. if (1) the powder contains hard phases so that their crystallite size cannot be reduced by milling and (2) the sample is in the form of compacted ceramic where milling is nearly impossible. Following results provide analysis for the last problem.

For the MgO-Y_2O_3 ceramic composites, Rietveld phase analysis gave relative weight fractions as shown in Table 3. The table also presents Rietveld absolute weight fractions which were computed using Eq. (2). Table 3 shows that the weight fraction calculations, using Eqs. (1) and (2), are inaccurate. The explanation for the inaccuracy is similar to the preceding samples. Eq.(2) has accommodated absorptive character, but still gave biased weight fractions. It should be noted, however, that both calculation models do not include either particle or crystallite size. Therefore, a new model is proposed to provide better accuracy.

Table 2. Absolute weight fractions of phases in MgO-α-Al_2O_3 powder mixtures calculated using Eq. (2) after Rietveld refinement. Estimated errors for the least significant digits are given in parantheses.

Sample		Milling time (hours)			
		0	1	2	3
PAKA	MgO	50,0(1)			
	α-Al_2O_3	49,0(1)			
PPKA	MgO	63,8(7)	58,5(8)	-	51,1(7)
	α-Al_2O_3	50,0(1)	50,0(1)	50,0(1)	50,0(1)
PAKP	MgO	50,0(1)	50,0(1)	50,0(1)	50,0(1)
	α-Al_2O_3	43,9(7)	48,3(7)	49,5(7)	49,9(7)

Table 3. Rietveld weight fractions in the MgO-Y_2O_3 ceramic composites calculated using the 'ZMV'methods and their biased figures. Estimated errors for the least significant digits are given in parantheses

Sample (MgO-Y_2O_3)	Relative weight fraction (%)		Bias in relative weight fraction		Absolute weight fraction (%)*		Bias in absolute weight fraction
	MgO	Y_2O_3	MgO	Y_2O_3	MgO	Y_2O_3	Y_2O_3
90-10	89.0(10)	11.0(2)	-1.0	+1.0	90.0(4)	14.2(3)	+4.2
80-20	82.3(10)	17.7(2)	+2.3	-2.3	80.0(4)	26.8(3)	+6.8
70-30	73.9(10)	26.1(3)	+3.9	-3.9	70.0(4)	45.7(6)	+15.7

The empirical proposed model to improve the absolute weight fraction calculation is given by

(6)

where D_i is the mean size of the crystallites of phase i which is calculated using Eq. (5) and D_T is threshold crystallite size which was determined independently and valued at approximately 50 Å.

Application of this model to the XRD data for the MgO-Y_2O_3 ceramic composites reduces the calculation biased for Y_2O_3 to 1.2%, 2.1% and 6.1%. The model was merely aimed to enhance accuracy by involving absorption coefficients as well as Rietveld crystallite size. As can be seen, the model can moderately improve the accuracy. Work is now underway to apply Eq. (4) as part of the model. Modification is required to be made to the model proposed by Taylor and Matulis (1991) [9] to give absolute weight fraction of phases.

4. Conclusion

Original approach of Rietveld phase analysis applied to x-ray diffraction data of presintered MgO-α-Al_2O_3 powder mixtures and sintered MgO-Y_2O_3 ceramic composites gave biased relative weight fraction of phases since it does not include the microabsorption effects. The bias is even larger when calculating absolute weight fraction where crystallite size effect is not accommodated. A new empirical model has been developed to give the correct concentrations with moderate accuracy, ie approximately by 6%. Further work is necessary to further improve the model.

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