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Summary Abstract - Quantitative Phase-Analysis of Partially Stabilized Zirconia-8.5-Percent Yttria by a Random Fitting Least Chi-Squared Method

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I. INTRODUCTION

Partially stabilized zirconia (PSZ-ZrO_2–8.5% Y_2O_3) is becoming the material of choice for thermal barrier coatings[1,2,3] because of its improved toughness and thermal fatigue resistance as compared to completely stabilized zirconia. Explanations for this improved toughness and thermal fatigue resistance[3–5,8] frequently include the relationship of the phase transformations among the tetragonal, cubic, and monoclinic phases to fracture and microcrack development along with the oxidation of the bond coating. As part of a larger study to understand the failure mechanisms of PSZ during thermal cycling, a new x-ray diffraction technique has been developed for the quantitative phase analysis of the three phases that can exist in PSZ. The major advantage of this technique is the improved accuracy with which the quantity of each phase can be calculated.

II. RANDOM FITTING LEAST CHI-SQUARED METHOD

The major problem in quantitative phase analysis of PSZ using x-ray diffraction is deconvoluting the overlapping cubic and tetragonal peaks. The (400) and (004) tetragonal peaks are separated by the (400) cubic peak as seen in Fig. 1. The procedure developed in this program consists of fitting each peak to an individual Gaussian function

$$F(x) = I \exp -\tfrac{1}{2}\,[(X - U)/V\,]^2,$$

where I is the maximum intensity of the Gaussian, U is the diffraction angle at which I occurs, V is the square root of variance of the function, and X is the diffraction angle 2θ and the independent variable. This technique is similiar to the technique developed by Shankar, Herman, Singhal, and Berndt.[6] For the three overlapping peaks three individual Gaussians are fit by adjusting the nine parameters that specify the functions. To accomplish this fit, a unique procedure was developed that utilized a random number generator to guess the values for each of the nine parameters simultaneously within prespecified limits. The goodness of fit for each guess was determined by comparing the measured data, that was an average of five independent experiments, with the predicted data using the chi-squared test.[7] The random number generator predictions are run several thousand times on the computer until an acceptable chi-squared value is generated.[7] Figure 2 presents the predicted best fit for the data presented in Fig. 1. In these figures the three peaks are clearly seen. When the individual Gaussian functions are known for each peak of the deconvoluted data, these functions can be integrated to determine the integrated intensity and the fraction of each phase can be calculated using standard techniques.[6,9] The (111) and (11$\bar{1}$) peaks are used for the monoclinic phase. The same random number generator and chi-squared test are easily used to determine the best Gaussian fit for these curves and their integrated intensity. The accuracy of this procedure depends first on the accuracy of the x-ray data and second on the accuracy of the fit of the data using the summation of the three Gaussians. The accuracy of the fit of the data is determined by the chi-squared goodness-of-fit test. In this procedure the values for the nine parameters are selected using the random number generator until the acceptability of the hypothesis[7] (i.e., accuracy of the fit) is greater than 99.5% as defined by the value of chi-squared and the number of degrees of freedom.[7]

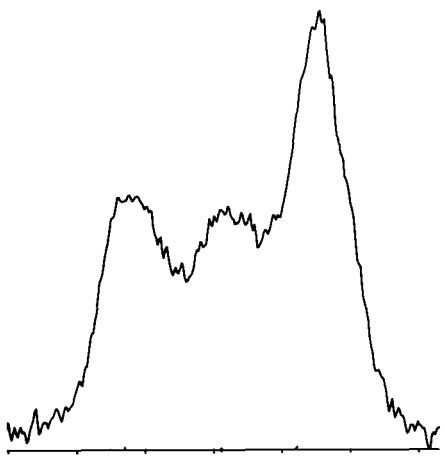

FIG. 1. Experimental x-ray intensity vs 2θ for the (400) cubic and (400), (004) tetragonal peaks.

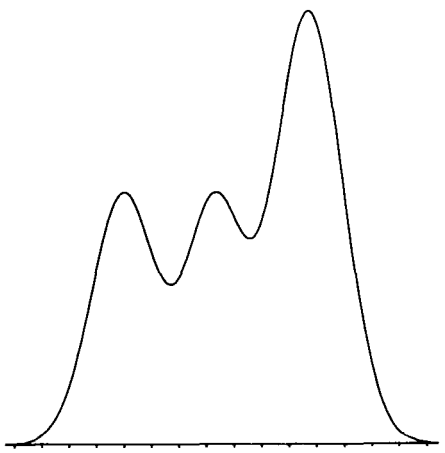

FIG. 2. Deconvoluted x-ray intensity for the data presented in Fig. 1.

TABLE I. Volume fraction of each phase determined by quantitative phase analysis of PSZ using random fitting chi-squared method.

	As received	Thermally cycled
Tetragonal (T)	80.0	78.9
Cubic (F)	18.4	20.7
Monoclinic (M)	1.6	<0.5
Chi squared	2.7	8.64
Degree of freedom[a]	49	49

[a] Degree of freedom is the number of observed points minus the number of parameters defined (Ref. 7).

III. EXPERIMENTAL RESULTS

Samples of PSZ powder ZrO_2–8.5 wt. % Y_2O_3 were used for this study. A quantity of this powder was thermally cycled between room temperature and 1300 °C in 10 min cycles for several hours. Samples of the as-received powder and the thermally cycled powder were analyzed using the above technique. The results are presented in Table I. The confidence in the calculated phase fractions can be determined using the value of chi-squared and the appropriate statistical tables.[7]

In Table I, it is seen that thermal cycling has reduced the quantity of monoclinic phase and the tetragonal phase with an increase in the cubic phase. Because of the uncertainty in the thermal condition of the as-received powder, it is currently not possible to discuss the phase transformations that have occurred in the powder during thermal cycling. However, the change in the fraction of each phase is accurate to the limits defined by the chi-squared value of the best fit of the Gaussians.

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