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Ceramics International 39 (2013) 197–202

CERAMICS INTERNATIONAL

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Application of response surface methodology (RSM) for optimization of sintering process for the preparation of magnesia partially stabilized zirconia (Mg-PSZ) using natural baddeleyite as starting material

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Received 7 May 2012; received in revised form 8 May 2012; accepted 2 June 2012
Available online 15 June 2012

Abstract

In this work, instead of chemical pure zirconia, natural baddeleyite was used as starting material to prepare partially stabilized zirconia (PSZ) with magnesia as stabilizer. Response surface methodology (RSM) involving central composite design (CCD) was employed to optimize the sintering process for the preparation of magnesia partially stabilized zirconia (MgO-PSZ) with the aim of improving the relative density and bending strength of the materials. The interaction between three variables i.e. sintering temperature, holding time and heating rate was studied and modeled. The statistical analysis of the results showed that in the range studied, sintering temperature had a significant effect on relative density and bending strength. The optimum combination predicted by RSM was experimentally confirmed, whereby almost complete densification with the relative density 99.44% was obtained at a 3 °C/min cooling rate.

Keywords: A. Sintering; Natural baddeleyite; Response surface methodology; Stabilizer

1. Introduction

Zirconia exhibits three polymorphs depending on temperature: monoclinic (m) up to 1170 °C, tetragonal (t) up to 2370 °C, and beyond this cubic (c) [1,2]. Pure zirconia can only be monoclinic at room temperature. In order to stabilize ZrO_2 in the tetragonal and/or cubic forms at room temperature and obtain sintered products with the best electrical and mechanical properties, it needs addition of different stabilizers such as MgO [3–5], CaO [6], Y_2O_3 [7], CeO [8,9], and even a combination of them [10,11].

Due to a wide range of applications, zirconia-based materials especially partially stabilized zirconia (PSZ) have received a great deal of attention. At present, the raw material which is used to prepare PSZ is usually chemical pure or industrial pure zirconia. Therefore, it not only increases the energy consumption and the cost, but also causes environmental pollution. In this work, PSZ is prepared by using natural baddeleyite as starting material, stabilized by the addition of magnesia. The natural baddeleyite was produced by floating baddeleyite ore.

In order to optimize the sintering process, the "response surface methodology" (RSM) has been used in our research. This method is used in empirical studies in order to evaluate the influence of some input parameters on a group of dependent variables that are significant for the process which is being studied [12]. In our work, three different sintering series (heating rate, sintering temperature and holding time) have been performed, and each sintered sample was characterized in terms of relative density and bending strength. The RSM was applied using the relative density and bending strength as dependent variables. In this way, it was possible to determine the best sintering process conditions.

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.06.009

2. Materials and experimental procedure

2.1. Materials

Instead of chemical pure zirconia, the natural baddeleyite powder (monoclinic ZrO_2) which was obtained after the floatation of baddeleyite ore was used as the starting material. The chemical composition of the natural baddeleyite powders with average size of 152 μm is shown in Table 1. The magnesium oxide was used as stabilizer with the addition of 3.0 wt% in this paper.

2.2. Experimental procedure

First of all is preparing sintering samples. The steps are shown as follows.

(1) Grinding: the natural baddeleyite powder was milled to average particle size of 5.67 μm using crusher.
(2) Ball milling: baddeleyite powder with average particle size of 5.67 μm was mixed with 3.0 wt% magnesium oxide powder. The mixtures were planetary milled using an agate ball (ball-feed weight ratio of 4–6:1) in ethanol for 24 h (average particle size 0.48 μm), and oven-dried at 80 °C for 10 h.
(3) Dry pressing: the mixture of magnesium oxide and zirconia was blended with a determined quantity of binder, and was uniaxially pressed at 150 MPa by single action at a constant strain for 8 min. The sizes of samples were 3 mm × 4 mm × 40 mm and Ø15 mm × 3 mm, respectively.

Then, the samples were heat treated at 850 °C in air at a heating rate of 5 °C/min for 4 h in order to burn out the binder. After the discharge treatment, the furnace was allowed to cool at the cooling rate of 5 °C/min. Finally, the samples were sintered at the designed experimental condition.

2.3. Experimental design

Before designing this experiment, suitable values for the three sintering factors, i.e. sintering temperature, holding time and heating rate were selected based on the preliminary study. Response surface method (RSM) is a solution to the problem of multi-variable statistical methods. Central composite design (CCD) is a kind of RSM. CCD with a full factorial was developed using the Design Expert software. Each factor is varied over three levels: the high level (+1), the low level (−1) and the center points (coded level 0). The processing factors and levels involved in the study are shown in Table 2.

CCD consisting of 6 center points and 14 axial points that rendered a total of 20 runs of experiment containing six replications was used to analyze the data acquired from the experimental runs. These data are then used to optimize sintering process. In our study, the response variables measured were relative density and bending strength.

Table 1
Chemical compositions of experimental material.

Powder material	Composite (wt%)			
Natural baddeleyite	ZrO_2+HfO_2 ≥ iOOr0%	SiO_2 ≤ iOOr%	Fe_2O_3 ≤ iOOr%	TiO_2 ≤ iOOr%

3. Results and discussion

CCD with a full factorial was developed using the Design Expert software. Each factor is varied over three levels: the high level (+1), the low level (−1) and the center points (coded level 0). The experimental results concerning relative density (Y_1) and bending strength (Y_2) using three factors CCD experimental design are shown in Table 3. The responses (Y_1, Y_2) are in the growth with sintering temperature in the given range. In contrast, the heating rate played a negative role on the responses. The growing tendency of the responses with holding time became flat after the holding time is up to 5 h.

Due to the analysis of the data of Table 3, the response Y_1 and Y_2 were fitted with second order polynomial equations:

$$Y_1(\text{relative density},\%) = -18.08469 + 0.14457A + 0.47426B + 0.38091C - 0.000075AB - 0.0002625AC + 0.010625BC - 0.0000446661A^2 - 0.035651B^2 - 0.010681C^2 \quad (1)$$

$$Y_2(\text{bending strength, MPa}) = -2039.97654 + 2.57445A - 1.43182B + 39.73952C + 0.011288AB - 0.030734AC + 0.047812BC - 0.000713089A^2 - 1.28227B^2 + 0.19774C^2 \quad (2)$$

The statistical significance of the models equations were evaluated by the F-values for analysis of variance (ANOVA). ANOVA evaluations of these models, shown in Table 4, implied that these models can describe the experiments, respectively. To measure how well the suggested models fit the experimental data, the parameters F-value, R^2, p-value, and lack of fit were used [13].

The ANOVA statistics for all the responses Y_1 and Y_2, shown in Table 4, indicated that these quadratic models could be used to navigate the design space. As can be seen in Table 4 the prob > F-values for relative density and

Table 2
Independent variables and their levels in the experimental design.

Symbol	Factors	Levels		
		−1	0	1
A	Sintering temperature (°C)	1450	1500	1550
B	Holding time (h)	3	4	5
C	Heating rate (°C/min)	3	5	7

Table 3
Experimental design and results of the central composite design.

Run	Variables			Response	
	Sintering temperature (°C) *A*	Holding time (h) *B*	Heating rate (°C/min) *C*	Relative density (%) Y_1	Bending strength (MPa) Y_2
1	1500	4	8.36	98.67	221.157
2	1450	3	3	98.36	215.894
3	1550	3	3	99.21	242.591
4	1500	4	5	99.03	233.573
5	1500	4	5	99.05	233.178
6	1450	5	3	98.52	220.284
7	1550	3	7	98.92	227.621
8	1450	5	7	98.42	217.99
9	1500	5.68	5	99.29	242.921
10	1500	4	5	99.01	232.157
11	1500	2.32	5	98.79	223.611
12	1550	5	7	99.15	234.651
13	1500	4	5	98.99	231.993
14	1500	4	5	98.97	230.717
15	1415.91	4	5	97.99	197.12
16	1550	5	3	99.43	259.003
17	1500	4	5	99.1	233.978
18	1450	3	7	98.1	203.453
19	1500	4	1.64	99.37	257.103
20	1584.09	4	5	99.66	266.581

Table 4
ANOVA analysis for responses Y_1 [relative density, %] and Y_2 [bending strength, MPa].

Source	Sum of squares	DF	Mean square	*F* value	Prob > *F*	
For Y_1						
Model	3.51	9	0.39	20.73	< 0.0001	Significant
Residual	0.19	10	0.019			
Lack of fit	0.18	5	0.035	16.49	0.004	Significant
Pure error	0.011	5	2.15E-03			
Adeq precision = 16.633						
For Y_2						
Model	5172.24	9	574.69	12.71	0.0002	Significant
Residual	452.05	10	45.21			
Lack of fit	444.76	5	88.95	61.01	0.0002	Significant
Pure error	7.29	5	1.46			
Adeq precision = 13.457						

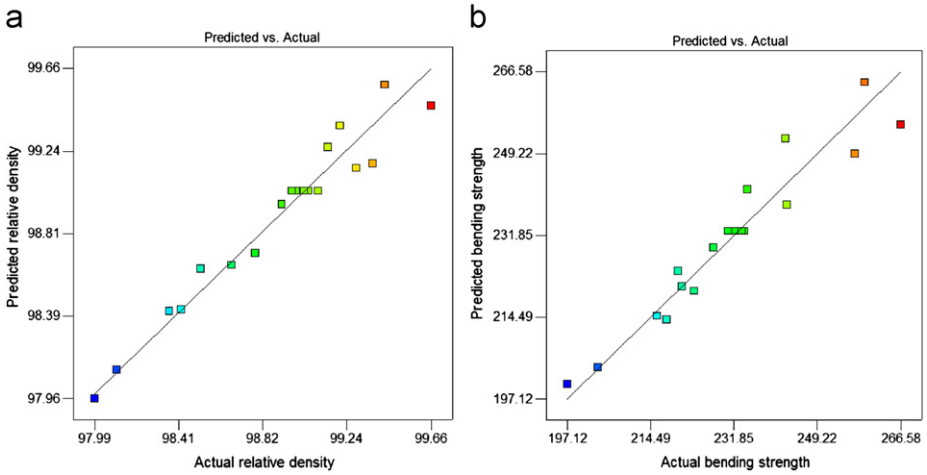

Fig. 1. Predicted versus actual. (a) Relative density and (b) bending strength.

bending strength were lower than 0.05 indicating that quadratic models were significant. The "lack of fit tests" compares the residual error to the "Pure Error" from replicated experimental design points. The *p*-values, greater than 0.05, for both the responses indicated that lack of fit for the model was insignificant. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is desirable. The adequate precision for Y_1 and Y_2 were 16.633 and 13.457, respectively. These high values of adequate precision demonstrated that models were significant for the process.

Usually it is essential to ensure that selected model is providing an adequate approximation to the real system. By applying the diagnostic plots such as the predicted versus actual value plot, the model adequacy can be judged. The correlation coefficient between actual and predicted values for Y_1 and Y_2 were 0.95 and 0.92, respectively. These R^2 values which were found to be close to 1 illustrated good agreement between the calculated and observed results within the range of experiment. As can be seen in Table 4, *F*-values which were 20.73 and 12.71 implied that the quadratic models were significant.

The actual and predicted relative densities and bending strengths were plotted in Fig. 1. The response surface plots for relative density and bending strength in Fig. 2 depicted the change of relative density and bending strength with sintering temperature, holding time and heating rate, plotted for the case where the cooling rate was 3 °C/min.

The sintering temperature and heating rate have different effects on the responses (relative density and bending

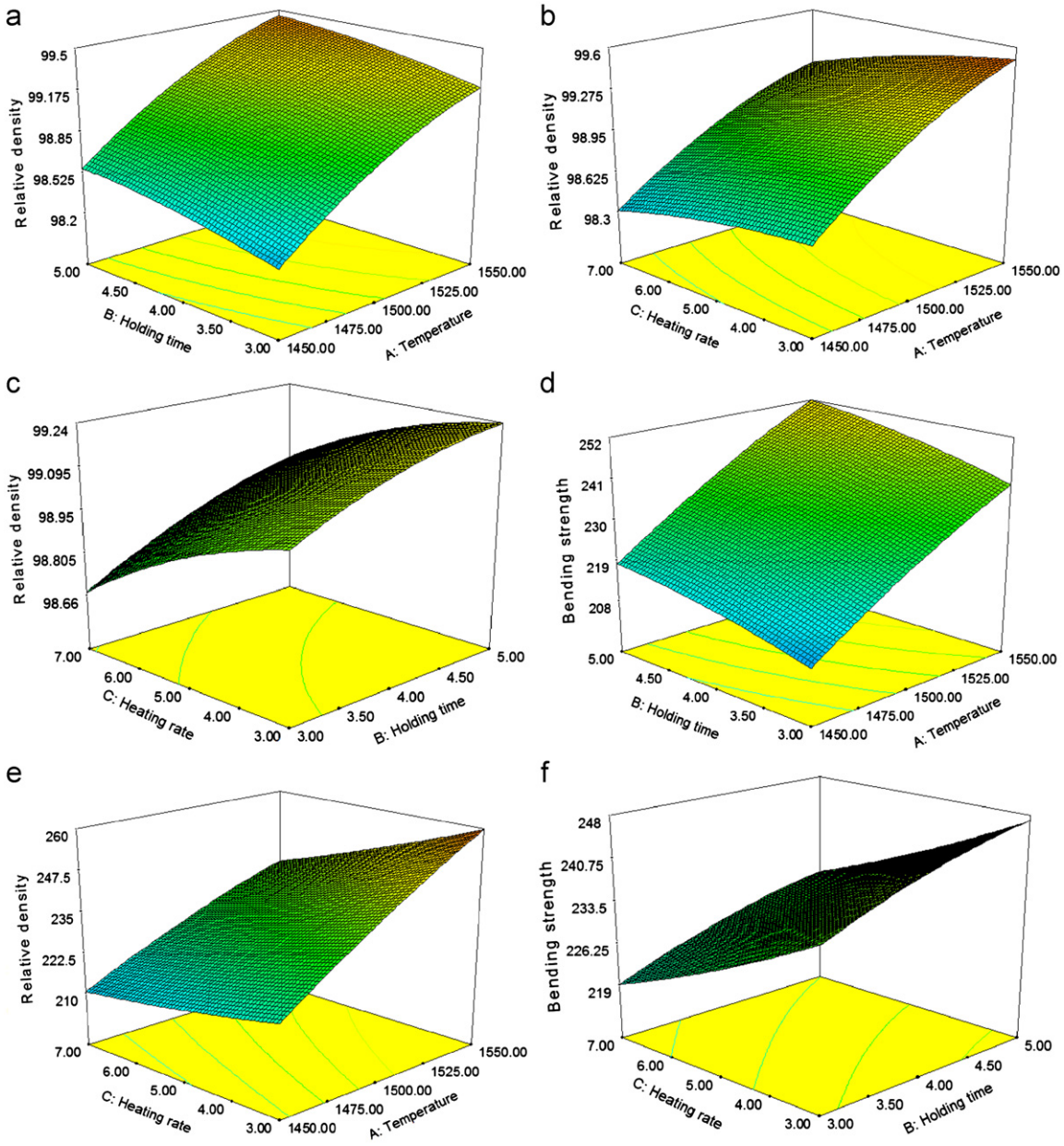

Fig. 2. Effect of sintering temperature, holding time and heating rate on relative density and bending strength.

strength). Sintering temperature is positive, heating rate is negative. High temperature and low heating rate were profitably for reducing bulk porosity so as to increase the relative density of sintered samples. The relative density and bending strength increased gradually with lengthened holding time and then became flat. That is because extending the holding time had nearly no effect on the responses (relative density and bending strength) when the transformation from monoclinic to tetragonal reaching equilibrium.

The mathematical model generated during RSM implementation was validated by conducting experiments on the given optimal medium setting. Process results of experimental optimization shown in Table 5 at the optimized parameters, implied that the predicted values were in good agreement with experimental values. The optimized parameters were sintering temperature of 1550 °C, holding time of 5 h, and heating rate of 3 °C/min.

The XRD spectrum and SEM images of samples sintered at the optimized process are shown in Figs. 3 and 4 respectively. By XRD spectrum, the monoclinic and tetragonal phases could be observed, which implied that partially stabilized zirconia was obtained after the sintering process.

The SEM images showed that the product obtained from the optimized process had a homogeneous structure and nearly no pore which could result in high relative density and good mechanical properties. This is because the samples before sintering typically contain dozens of air holes, and there are only point contact between particles. However, high temperature would result in contact area expansion, particles gathering and volume contraction. And grain boundaries form with the shortening of distance between particles. In the meantime, the air holes become isolated from being connected, gradually reduced, and escaped at high temperature. Therefore, the densification of the PSZ was achieved eventually with fine homogeneous structure.

Table 5
Validation experiment.

Relative density(%)			Bending strength (MPa)		
Predicted value	Actual value	Residual	Predicted value	Actual value	Residual
99.5745	99.44	0.14%	264.298	260.763	1.36%

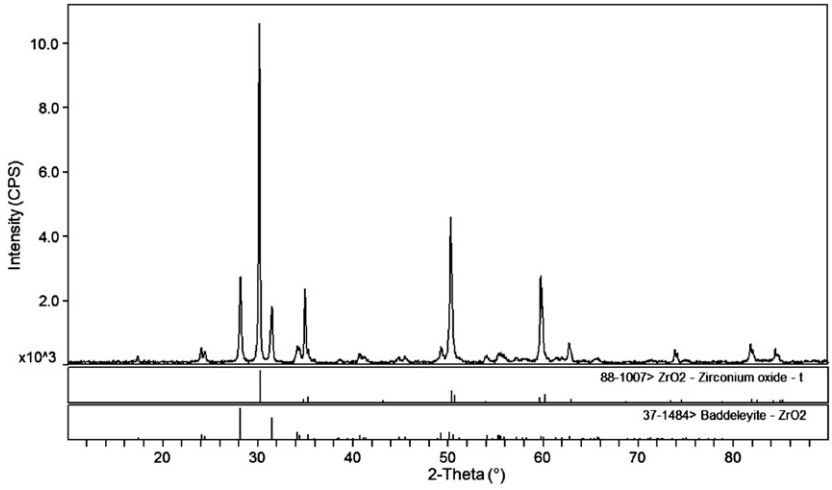

Fig. 3. XRD of samples sintered at the optimized process.

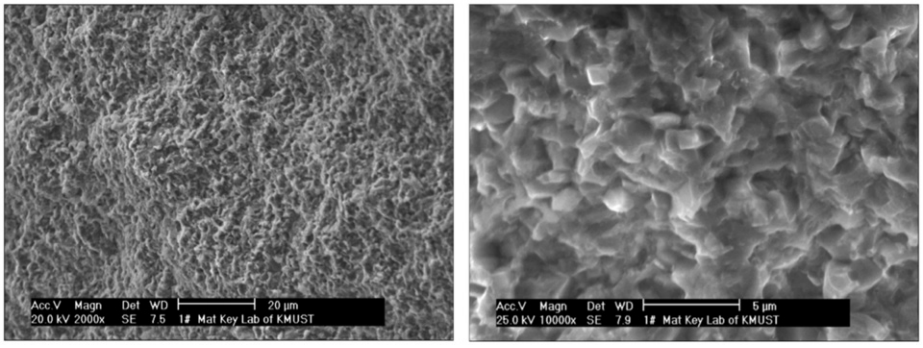

Fig. 4. SEM images of samples sintered at the optimized process.

4. Conclusions

(1) In this paper the natural baddeleyite which was obtained by floating of baddeleyite ore, was used as the starting material to prepare partially stabilized zirconia instead of chemical pure zirconia. Therefore, it can shorten the process and reduce energy consumption.
(2) Response surface methodology (RSM) was successfully applied to determine the optimum operational conditions for the properties of MgO-PSZ (e.g. relative density, bending strength, etc.) The temperature, 1550 °C; holding time, 5 h; and heating rate, 3 °C/min were found to be the optimum conditions to achieve the maximum relative density and bending strength of MgO-PSZ. Two quadratic models, developed in terms of sintering temperature, heating rate and holding time to represent the relative density and bending strength and corresponding coefficients of independent variables were estimated by the application of the Design Expert software. The response evaluated from the quadratic models shows a good agreement with the observed ones.

Acknowledgment

This work was supported by the International S&T Cooperation Program of China (No. 2012DFA70570), the Yunnan Provincial International Cooperative Program (No. 2011IA004), and Project (51090385) supported by the National Natural Science Foundation of China.

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