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Ceramics International 39 (2013) 1525–1531

CERAMICS INTERNATIONAL

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Effects of in situ synthesized mullite whiskers on flexural strength and fracture toughness of corundum-mullite refractory materials

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Received 17 July 2012; accepted 30 July 2012
Available online 8 August 2012

Abstract

The method of in situ synthesis of mullite whiskers was introduced to improve the fracture toughness of the corundum-mullite refractory materials. Effects of process parameters (sintering temperature, holding time and addition amount of V_2O_5) on flexural strength and fracture toughness of corundum-mullite during the in situ toughening course were analyzed. The optimum process parameters (the sintering temperature of 1350 °C, the holding time of 2 h, and the V_2O_5 addition amount of 5%) for in situ synthesized mullite whiskers to toughen corundum-mullite were obtained by the response surface method combined with single factor analysis. SEM and EDS analysis results demonstrated that the mullite whiskers had been synthesized in corundum-mullite and they could bridge the cracks during the fracture process. After in situ toughening, the flexural strength versus deflection curves of corundum-mullite showed obvious zigzag or waveform characteristics, indicating in situ toughening effects. At the same time, the flexural strength and corresponding deflection increased remarkably.

Keywords: Corundum-mullite; In situ toughening; Whiskers; Fracture toughness

1. Introduction

Corundum-mullite has been widely employed as a high quality refractory material because of its high mechanical strength, excellent corrosion resistance, high heat and creep resistance at high temperature, and so on [1]. However, it is also facing severe challenges due to its harsh service environment in the modern manufacture process. For example, the rate of rise and drop in temperature for corundum-mullite heated by microwave energy with high power can reach up to several hundred degrees per minute [2]. This intense heat shock can lead to failure or cracking of this refractory. So it is significant to toughen the corundum-mullite and improve its thermal shock resistance and service life through adequate processes [3].

In fact, many methods, including phase transformation toughening, particle dispersion toughening as well as fiber or whisker toughening, have been used to toughen the refractory materials in many researches [4]. Compared with above mentioned methods, it is low cost and more effective to toughen the refractory through in situ synthesized whiskers for the better dispersion of whiskers and no necessity of external whisker addition [5]. When the whiskers are pulled out and bridging cracks during the fracture process, the cracks can be deflected and the energy can be absorbed, consequently leading to the improvement of fracture toughness for ceramics or refractory materials [6]. In terms of corundum-mullite system studied in present study, it has been well documented that the synthesis of mullite whiskers is more convenient than that of corundum whiskers [7]. So, in situ synthesized mullite whiskers were chosen as the toughening phase in this paper.

Regarding with the synthesis of mullite whiskers, several routes have been investigated, such as gel or powder calcination, mineral decomposition and molten salt assisted synthesis [8,9]. Considering synthesis cost, more and more

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http://dx.doi.org/10.1016/j.ceramint.2012.07.101

mineral and industrial by-product has been applied to synthesize mullite whisker in recent years. For example, Park [10] has manufactured mullite whiskers with a diameter of 0.6–1.8 μm and aspect ratio larger than 30 by firing compacts of coal fly ash and $NH_4Al(SO_4)_2$ powders at 1300 °C for 10 h. In respect of toughening ceramics through in situ synthesized mullite whisker, Okada [11] has toughened tetragonal zirconia polycrystal(TZP) through in situ synthesized mullite whiskers and the fracture toughness of the composites shows a clear enhancement compared with that of pure TZP.

In present study, chemical pure $Al(OH)_3$ and SiO_2 powders were used to prepare corundum-mullite refractory materials, AlF_3 and V_2O_5 powders were used as sintering assistant agents to synthesize mullite whiskers. Then the mullite whiskers were synthesized and their effects on the flexural strength and fracture toughness of corundum-mullite were discussed.

2. Experimental

2.1. Material preparation

Chemical pure $Al(OH)_3$ and SiO_2 powders with a mean particle size less than 1.5 μm and a purity of 99.9% were used to prepare the corundum-mullite as raw materials, the AlF_3 and V_2O_5 powders were added as assistant agents for in situ synthesis of mullite whiskers. The ratio between corundum and mullite in this refractory was kept at 1:1 by weight through controlling the mixture ratio of raw materials. A wet ball-milling process was conducted for 24 h after proper amount of assistant agent was added into raw materials. After drying, the mixed powders were crushed in an agate mortar and passed through a 200 mesh sieve. Prismatical compacts with a dimension of 3 mm × 4 mm × 36 mm were prepared through die pressing. The compacts were placed in a closed alumina crucible and sintered at different temperatures for different holding time. According to previous research work [12], the optimum addition amount of AlF_3, i.e. 3 wt%, has been determined. So, the present paper is focusing on effects of sintering temperature, holding time and addition amount of V_2O_5 on the flexural strength and fracture toughness of the corundum-mullite after in situ toughening.

2.2. Analysis and test methods

The flexural strength of the corundum-mullite was measured using the three-point flexure test method on a WD-10 electron universal tester. The fracture toughness was evaluated using the single edge notched beam (SENB) method [13]. The samples with a dimension of 3 mm × 4 mm × 36 mm were polished by diamond cream before fracture toughness test. During fracture toughness test, the span was 30 mm and the loading rate was 0.05 mm/min^{-1}. The depth of the incision was 1 mm and the width was 0.2 mm. The morphologies of the in situ synthesized mullite whiskers and the microstructure of the sintered composite were observed by a scanning electron microscope (JEOL JSM-840 SEM), while the composition of mullite whiskers was analyzed by the energy disperse spectrum (EDS) technique. The crystalline phases of the sintered samples were identified by Philip 1140/00 XRD diffractor.

3. Results and discussion

Effects of process parameters (sintering temperature, holding time and addition amount of V_2O_5) on the flexural strength and fracture toughness of corundum-mullite during the course of in situ toughening were discussed. In the first stage, every single factor was analyzed, while others were fixed at the optimum values based on single factor analysis [12]. And then the interaction between different factors was analyzed by means of response surface methodology [14].

3.1. Effects of sintering temperatures on flexural strength

The flexural strength versus deflection curves of corundum-mullite samples sintered at different temperatures exhibit remarkable zigzag or waveform characteristics (see Fig. 1). The fracture mode of corundum-mullite after in situ toughening shows some ductile characteristics, which is obviously different from the brittle fracture mode of common untoughened refractory materials [5]. The zigzag or waveform characteristics in flexural strength versus deflection curves are mainly attributed to the roles of in situ synthesized whiskers. When the whiskers are pulled out from matrixes or bridging cracks, the energy

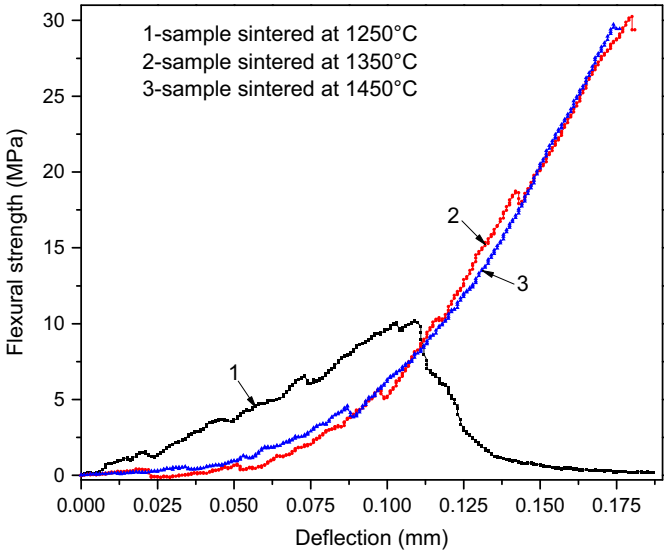

Fig.1. Flexural strength versus deflection curves of corundum-mullite samples sintered at different temperatures (Other process parameters: the addition amount of AlF_3 is 3 wt%, the addition amount of V_2O_5 is 5 wt%, and the holding time is 2 h).

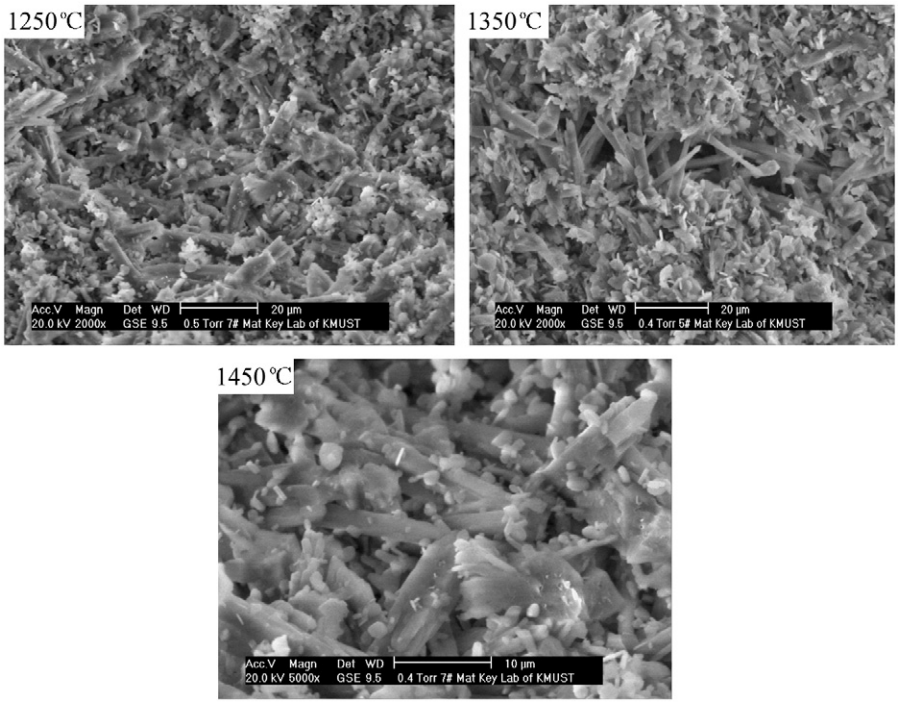

Fig. 2. SEM morphologies of fracture surface of corundum-mullite samples sintered at different temperatures.

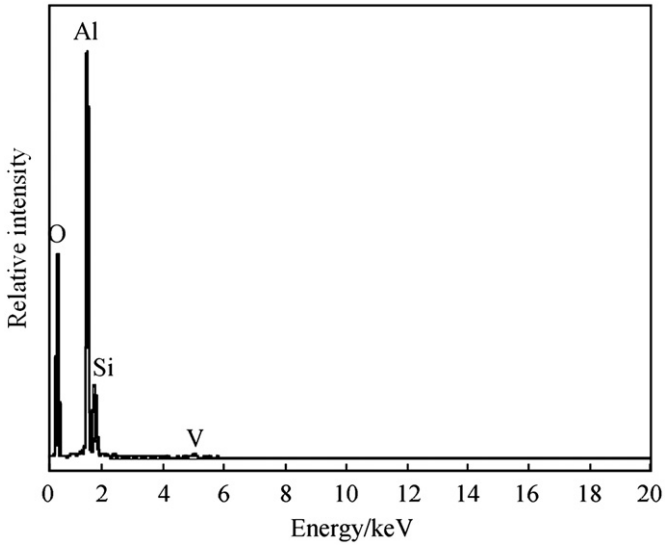

Fig. 3. EDS analysis result of in situ synthesized whiskers.

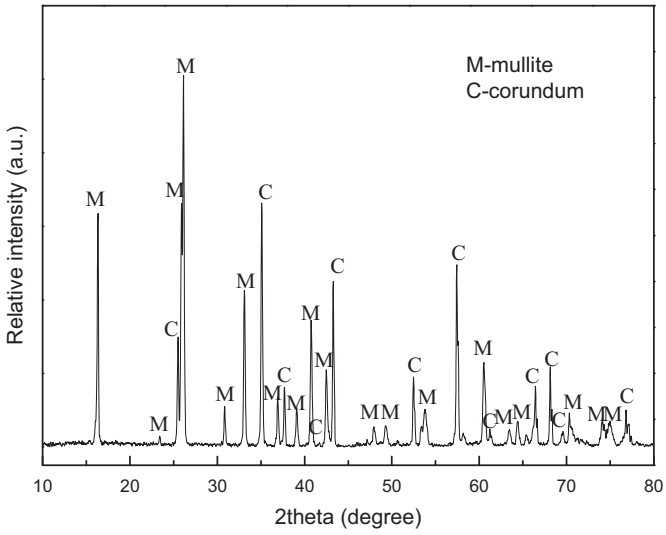

Fig. 4. XRD patterns of corundum-mullite refractory materials.

absorption or crack deflection will occur so that the brittle fracture can be avoided.

Fig. 2 exhibits the SEM morphologies of in situ synthesized whiskers in the fracture surface of corundum-mullite sintered at different temperatures. In the fracture surface of corundum-mullite sample sintered at 1250 °C, the needle-like crystalline grains are inclined to grow, but no whiskers have been synthesized completely. For the sample sintered at 1350 °C, numerous whiskers can be found in the cracks or pores on the fracture surface. The diameters of these whiskers range from 800 nm to 1 μm, while the length can reach up to about 20 μm. EDS analysis in Fig. 3 demonstrates that the composition of in situ synthesized whiskers agrees with the chemical constitution of mullite except some residual vanadium element, which originates from the remains of V_2O_5 after its volatilization [15]. According to the XRD results in Fig. 4, there are only corundum and mullite in the material and no other phases are detected. For the sample sintered at 1450 °C, the aspect ratio as well as the quality of synthesized whiskers decreases, as shown in Fig. 2.

The microstructure characteristics in Fig. 2 lead to another difference in the flexural strength versus deflection curves for

samples sintered at different temperatures. The peak flexural strength and corresponding deflection for the sample sintered at 1250 °C is the lowest, due to the high porosity of corundum-mullite matrix and no formation of mullite whiskers at low sintering temperature. The matrix of corundum-mullite becomes denser as the sintering temperature increases from 1250 to 1350 °C and many mullite whiskers have been synthesized (Fig. 2). So the flexural strength and corresponding deflection of the sample sintered at 1350 °C increase obviously. A further increase of temperature up to 1450 °C does not lead to further increase in flexural strength and deflection (Fig. 1), because the quality of whiskers decreases, as demonstrated in Fig. 2. Through above analysis, the optimum sintering temperature is 1350 °C.

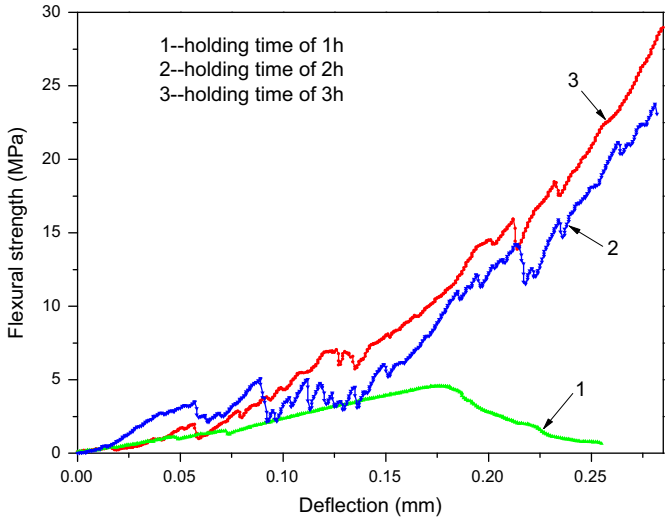

Fig. 5. Flexural strength versus deflection curves of corundum-mullite samples held for different time (Other process parameters: the addition amount of AlF_3 is 3 wt%, the addition amount of V_2O_5 is 5 wt%, and the sintering temperature is 1350 °C).

In general, the flexural strength of corundum-mullite samples sintered between 1250 and 1450 °C is still much lower than the theoretical strength because of the existence of pores. But on the other hand, the existence of pores is necessary for the synthesis of mullite whiskers, because the synthesis process is a gas–solid reaction with the aid of the volatilization of AlF_3 and V_2O_5. These pores are favorable to gas diffusion and whisker synthesis. The fracture toughness is more significant than absolute strength for applications of some refractory materials [3]. So the method of in situ synthesis of whiskers can be employed to toughen the corundum-mullite although its flexural strength is still lower after in situ toughening.

3.2. Effects of holding time on flexural strength

Fig. 5 shows the characteristics of flexural strength versus deflection curves of corundum-mullite sintered for different holding time at 1350 °C. For the sample held 1 h, the flexural strength is too low, only being of 5 MPa. The flexural strength versus deflection curve does not exhibit zigzag or waveform characteristics, and the fracture mode of the sample is still brittle fracture. The mullite whiskers are not observed on the fracture surface for the sample held 1 h in SEM morphologies (Fig. 6), because the holding time of 1 h is too short for the adequate synthesis of mullite whiskers, resulting in the lower flexural strength and no toughening effects.

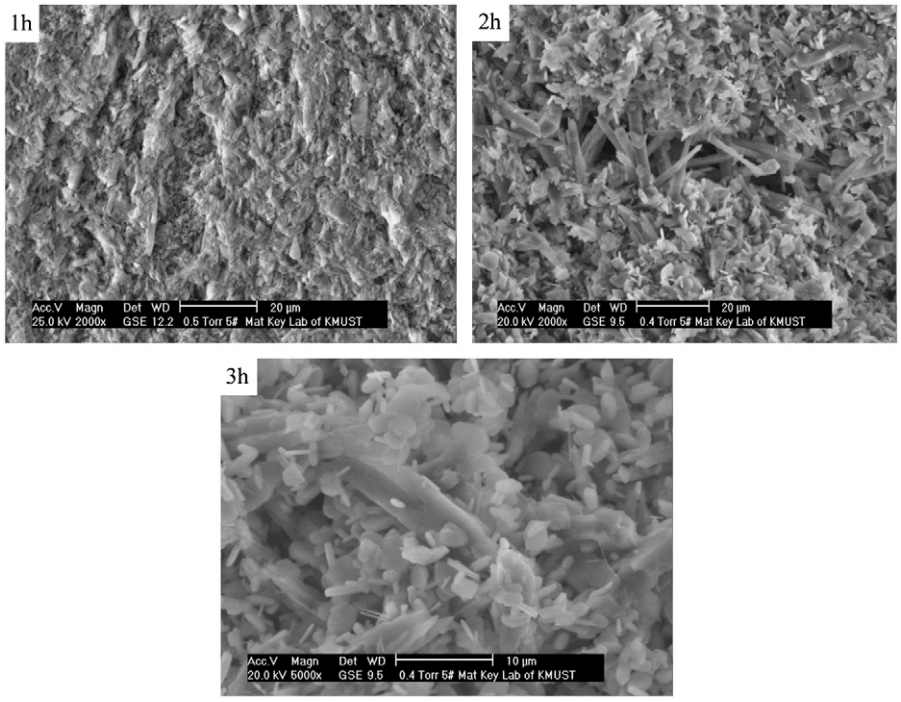

Fig. 6. SEM morphologies of fracture surface of corundum-mullite samples held for different time.

The mullite whiskers have been synthesized on the fracture surface for sample held 2 h and they can bridge the cracks (Fig. 6), which directly leads to the appearance of zigzag or waveform characteristics in the curve of flexural strength versus deflection (Fig. 5). The porosity of corundum-mullite matrix decreases as the holding time increases from 1 to 2 h, and the flexural strength increases accordingly. When the holding time is further increased to 3 h, the aspect ratio of the mullite whisker decreases and a large number of whiskers have further grown and become flake grains (Fig. 6). As a result, the toughening effects do not increase obviously when the holding time increases from 2 to 3 h.

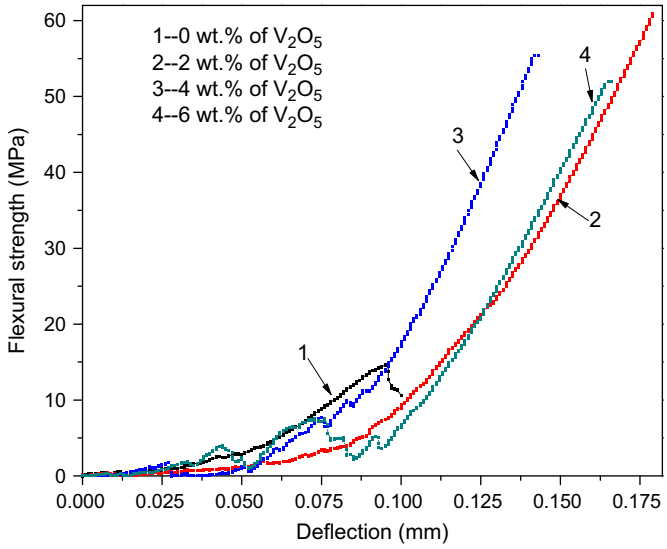

Fig. 7. Flexural strength versus deflection curves of corundum-mullite samples with different addition amounts of V_2O_5 (Other process parameters: the addition amount of AlF_3 is 3 wt%, the sintering temperature is 1350 °C, and the holding time is 2 h).

3.3. Effects of V_2O_5 addition on flexural strength

The flexural strength is only 15 MPa and the curve of flexural strength versus deflection does not show zigzag or waveform characteristics as well as corresponding toughening effects for the sample without V_2O_5 addition (Fig. 7). SEM morphologies in Fig. 8 indicate that there are not mullite whiskers on the fracture surface, demonstrating that the V_2O_5 addition is indispensable for the synthesis of mullite whiskers. So the low strength and no toughening effects appear for the sample without V_2O_5 addition [15].

When the addition amount of V_2O_5 increases from 0% to 2%, the mullite whiskers can be synthesized and they bridge the cracks during the fracture process (Fig. 8). As a result, zigzag or waveform characteristics for the flexural strength versus deflection curves appear in Fig. 7. The flexural strength of this sample increases from 15 to 60 MPa and the deflection increases by 100% (Fig. 7). The increase in V_2O_5 addition amount from 2% to 4% leads to a further increase in the flexural strength (Fig. 7). When the addition amount of V_2O_5 reaches up to 6%, the flexural strength of the sample decreases a little in the opposite way. During the mullite whisker synthesis, the volatility of V_2O_5 will create pores in corundum-mullite matrix. So the sample with high addition amount of V_2O_5 shows low flexural strength although numerous mullite whisker are synthesized (Fig. 8).

3.4. Effects of process parameters on fracture toughness of corundum-mullite

In above discussion, when the effects of one single factor were analyzed, the values of other factors were fixed. In

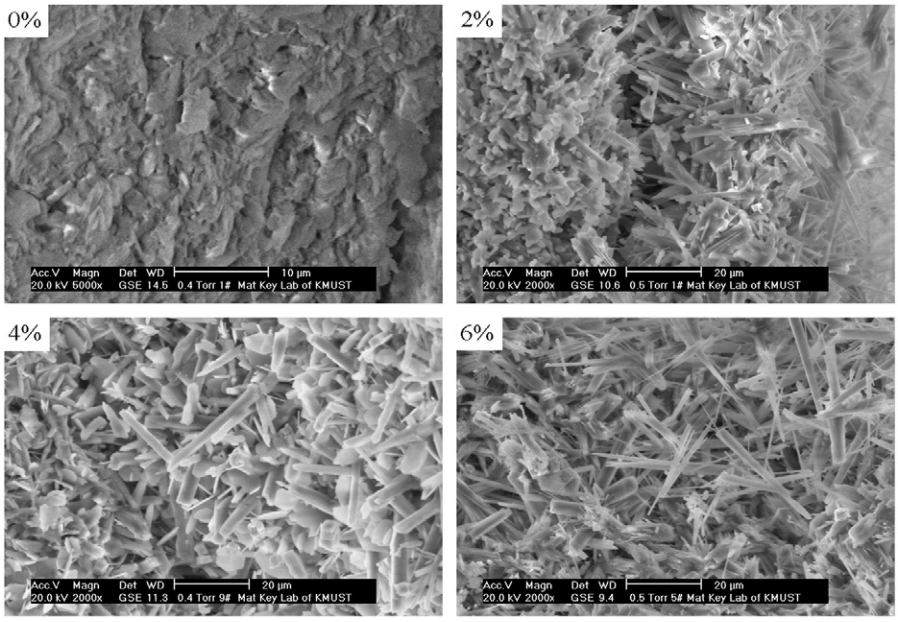

Fig. 8. SEM morphologies of fracture surface of corundum-mullite samples with different addition amount of V_2O_5.

this section, the response surface method (RSM) was used in order to consider the interaction between different factors [15]. At the same time, the fracture toughness of corundum-mullite was measured to evaluate the toughening effects quantitatively.

It can be found in Fig. 9 that the fracture toughness of corundum-mullite increases firstly and then decreases in the temperature range from 1250 to 1450 °C and the optimum sintering temperature is about 1350 °C. Effects of holding time on fracture toughness are similar to those of temperature (Fig. 9). The optimum holding time is 2 h. The analysis result based on RSM about the effects of sintering temperature and holding time on fracture toughness agrees with that of one single factor analysis.

Effects of sintering temperature on fracture toughness in Fig. 10 are same as that in Fig. 9, and the optimum sintering temperature is about 1350 °C. But on the contrary, the fracture toughness keeps a continuous increase as the addition amount of V_2O_5 increases from 2% to 6%. When the addition amount of V_2O_5 is more than 5%, the increase rate of toughness becomes much lower. So the effects of V_2O_5 addition on fracture toughness are not significant when the addition amount is more than 5%, agreeing with that of single factor analysis (Fig. 7).

4. Conclusions

The following conclusions can be drawn through investigations of effects of in situ synthesized mullite whiskers on the flexural strength and fracture toughness of corundum-mullite:

(i). The mullite whiskers could be in situ synthesized in pores or cracks of corundum-mullite and they could bridge the cracks during the fracture process.

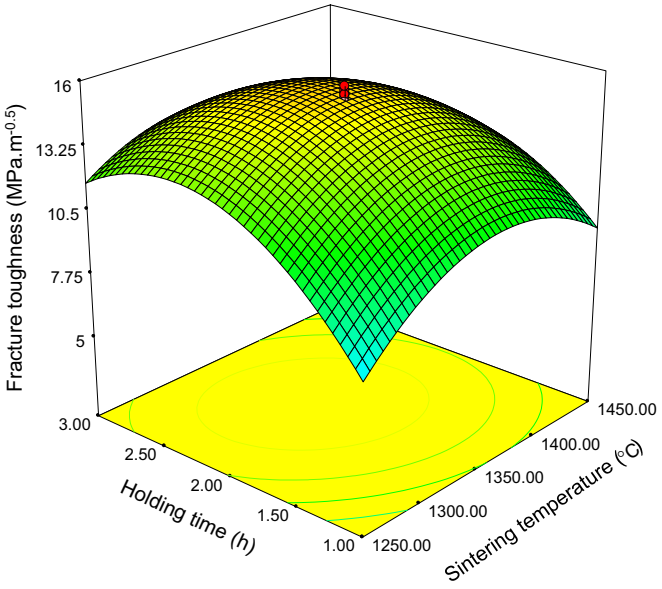

Fig. 9. Effects of sintering temperature and holding time on fracture toughness by means of RSM.

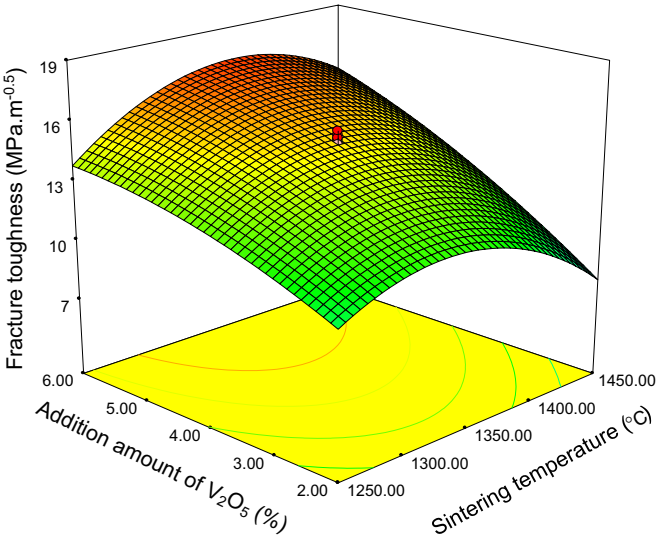

Fig. 10. Effects of V_2O_5 addition and sintering temperature on fracture toughness by means of RSM.

(ii). The flexural strength versus deflection curves of corundum-mullite showed obvious zigzag or waveform characteristics and toughening effects after in situ toughening. The flexural strength and corresponding deflection improved remarkably.

(iii). The optimum process parameters for in situ synthesized mullite whiskers to toughen corundum-mullite obtained by the response surface method combined with single factor analysis were the sintering temperature of 1350 °C, the holding time of 2 h, and the V_2O_5 addition amount of 5%.

Acknowledgments

The authors acknowledge the financial supports from the National Scientific Foundation of China (No. 51102123), the International S&T Cooperation Program of China (No. 2012DFA70570), the Yunnan Provincial International Cooperative Program (No. 2011IA004), the Doctoral Fund of Youth Scholars of Ministry of Education of China (20105314120002) and the Applied Foundation Fund of Yunnan Province of China (2009ZC012M).

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