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Ceramics International 39 (2013) 1299–1305

CERAMICS INTERNATIONAL

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Microstructure and properties of pore-created SiC ceramics with calcium chloride as pore former

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Received 2 June 2012; received in revised form 18 July 2012; accepted 19 July 2012
Available online 24 July 2012

Abstract

Pore-created silicon carbide (SiC) ceramics were liquid phase sintered (LPS) by using Al_2O_3–Y_2O_3 as sintering additive and calcium chloride ($CaCl_2$) as pore former. The $CaCl_2$ did not react with other compositions, and accumulatively formed $CaCl_2$ crystals on the grain boundary of SiC ceramics. The addition of $CaCl_2$ decreased the sintering and mechanical properties of SiC ceramics, but obviously reduced the dry friction coefficient. The pores on the surface and inside of SiC ceramics could be continuously created by the solubility and non-volatility of calcium chloride.

Keywords: C. Mechanical property; Silicon carbide; Ceramic matrix composite

1. Introduction

Silicon carbide (SiC) ceramic is a well-known structural material and possesses remarkable mechanical and thermal properties, such as high hardness, high specific strength, corrosion resistance, high thermal stabilities [1–5]. SiC ceramic has been widely used in all kinds of sliding-wear applications, such as bearing, wear parts, valves, and seals [6–11]. In particular, it has made great contributions for sealing of mechanical devices in harsh working conditions [8–11].

During the sealing, it is inevitable to generate wear fragments from sealing materials. In addition, liquid mediums, such as lubricants and coolants, possibly contain some solid particles. If the wear fragments and solid particles are not removed from seal faces timely, the abrasive wear and heat cracking will occur, which speeds up the wear and worsens the sealing performance and service life [11]. The effective method to solve the problem is to form pores on the seal faces. The surface pores can not only increase the flexibility, improve the thermal shock resistance and reduce the friction coefficient, but also store liquid mediums, fragments or solid particles during the sealing. It improves the friction performances of the seals, and prolongs the service life [12].

At present, a main approach to create pores on the SiC seal face is to produce the spherical pores by special processing methods, such as laser machining, electrical discharge machining, ultrasonic machining, electrochemical machining, electron beam processing and so on [12–14]. These machining methods can control the size, depth and shape of the pores, but they are expensive, energy-consuming and low productive due to high hardness of SiC. When the processed pores are exhausted, the seals face has to be re-processed. In addition, the processing will decrease the mechanical properties of SiC seals.

Another possible approach to create pores on the seal face is to prepare porous silicon carbide ceramics by adding pore-forming materials. At present, there are many researches on the fabrication of porous SiC ceramics by oxidization, decomposition and volatilization of volatile pore-forming materials [15–21]. The volatile pore-forming materials include ammonium carbonate, ammonium bicarbonate, ammonium chloride, inorganic carbon coal, carbon powder, natural fibers, polymer, PMMA spheres and so on. However, the most obvious defect of pore-creation by volatilization is to drastically decrease the mechanical properties owe to the existence of pores on the surface and inside the sintered body. It is reason why the present

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http://dx.doi.org/10.1016/j.ceramint.2012.07.064

pore-creation on the SiC seal face still adopts special and expensive surface machining methods.

The new pore-creation method that corresponds to volatilization is pore-creation by non-volatilization. That is non-volatile pore formers are used to create pores, they will not decompose or little volatilize during the sintering, but they can dissolve in some solvents at room temperature. The surface pores can be obtained by washing and solving of non-volatile pore formers during finishing. Compared with pore-creation by volatilization, the non-volatile pore formers still exist inside the sintered body, which will improve the decrease extent of mechanical properties due to the addition of pore formers.

The aim of this work was to create the pores on the surface of SiC ceramics by using calcium chloride ($CaCl_2$) as non-volatile pore former. The SiC ceramics containing $CaCl_2$ were liquid phase sintered (LPS) by using Al_2O_3 and Y_2O_3 as sintering additive. The effects of $CaCl_2$ on the sintering behaviour, microstructure, and mechanical and friction properties of LPS–SiC ceramics were investigated.

2. Experimental

2.1. Processing

The raw materials used in this experiment were SiC powder (provided by Taizhou Dongxin Seal Limited Company, purity >98.5%), Al_2O_3 powder (purity >99%), Y_2O_3 powder (purity >99%) and $CaCl_2$ powder (purity >99%), in which, Al_2O_3 and Y_2O_3 were used as sintering additive, and $CaCl_2$ as non-volatile pore former. The compositions of all batches were listed in Table 1. In the procedure, SiC, Al_2O_3, Y_2O_3 and $CaCl_2$ were mixed and ball-milled for 6 h in a steel container using silicon carbide balls and **de-ionized** water as grinding media. The SiC slurry with 40% solid content was obtained, and then dried to SiC granules by spray-drying method [22–24]. The SiC granules were compacted into green bodies by two-directional compaction technology at 20–100 MPa. Then isostatic pressing was conducted on green bodies at 150–200 MPa. Liquid phase sintering was conducted in a vacuum furnace at 1850 °C for 1 h, which coincided with Ref. [25]. After the sintering, the samples were finished by machining and washing.

Table 1
Compositions of all batches.

No.	SiC/wt%	$Al_2O_3+Y_2O_3$/wt%	$CaCl_2$/wt%
C0	90	10	0
C5	85	10	5
C10	80	10	10
C15	75	10	15
C20	70	10	20

2.1.1. Properties and microstructure characterization

The bulk density of the samples was measured by the conventional water-displacement method. The phase compositions were analyzed by the X-ray diffractomer (Rigaku D/max-RA, XRD). The surface and fracture morphologies of the sintered bodies were observed by scanning electron microscopes (HITACH IS-4800). The bending strength was measured by electronic universal test machine (CMT5205) with span of 30 mm and the cross-head speed of 0.5 mm/min. The hardness was measured by the

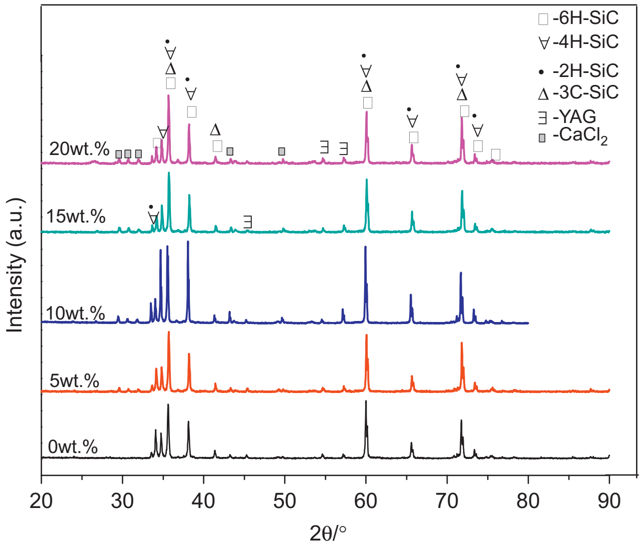

Fig. 2. X-ray diffraction patterns of LPS–SiC ceramics containing calcium chloride.

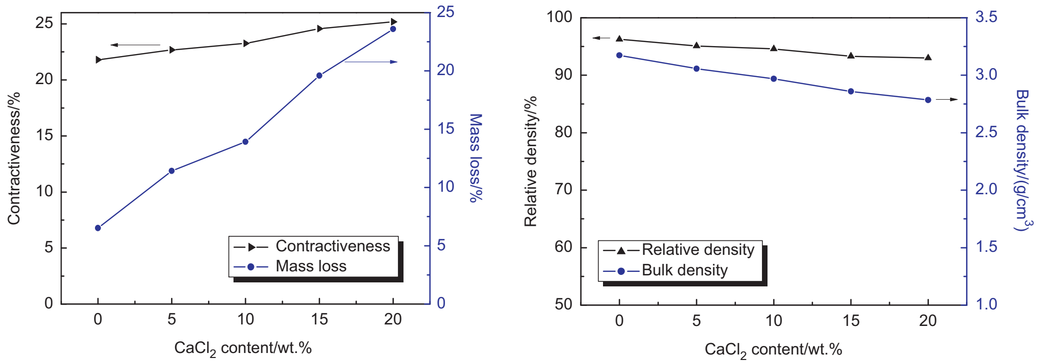

Fig. 1. Sintering behaviour of LPS–SiC ceramics containing calcium chloride.

Vickers indenter (Hv-10 A) with 10 kg load. The dry friction coefficient was measured by the friction and wear spectrometer (WTM-1E) with standard load of 100 *g*, friction speed of 300 R/min and friction orbit radius of 6 mm.

3. Results and discussion

3.1. *Effect of $CaCl_2$ on sintering behaviour*

As known, sintering is not only related to the densification of ceramics, but also to the size of crystals and the volatilization of compositions. In this work, liquid phase sintering was used to densify SiC ceramic by using Al_2O_3 and Y_2O_3 as sintering additive. The formation temperature of $Y_3Al_5O_{12}$ (the mole ratio of Y:Al is 3:5) is about 1760 °C [25]. The melting and boiling points of $CaCl_2$ are 772 and 1935 °C, respectively [26]. Therefore, sintering temperature should be limited in 1760–1935 °C, which achieves the densification of SiC ceramic and simultaneously restricts the volatilization of $CaCl_2$. According to the previous researches on LPS–SiC ceramics [21–25], the sintering temperature of 1850 °C was chosen in the experimental.

The sintering behaviour of LPS–SiC ceramics containing $CaCl_2$ are shown in Fig. 1. With the increase of $CaCl_2$ content, the contractiveness and mass loss constantly increase, and the density basically decreases. When the $CaCl_2$ content increases from 0 to 20 wt%, the contractiveness and mass loss of sintered sample increase from 21.80% and 6.52% to 25.18% and 23.60%, respectively, and the bulk density of SiC ceramic decreases from 3.17 to 2.78 g/cm^3. It indicates that calcium chloride worsens the sintering properties of SiC ceramics.

Calcium chloride has high water absorption, and can maximally adsorb six H_2O molecules. There exists much adsorbing water on the surface of SiC granules and green body, the amount of adsorbing water increases with the $CaCl_2$ content. At the same time, $CaCl_2$, Al_2O_3 and Y_2O_3

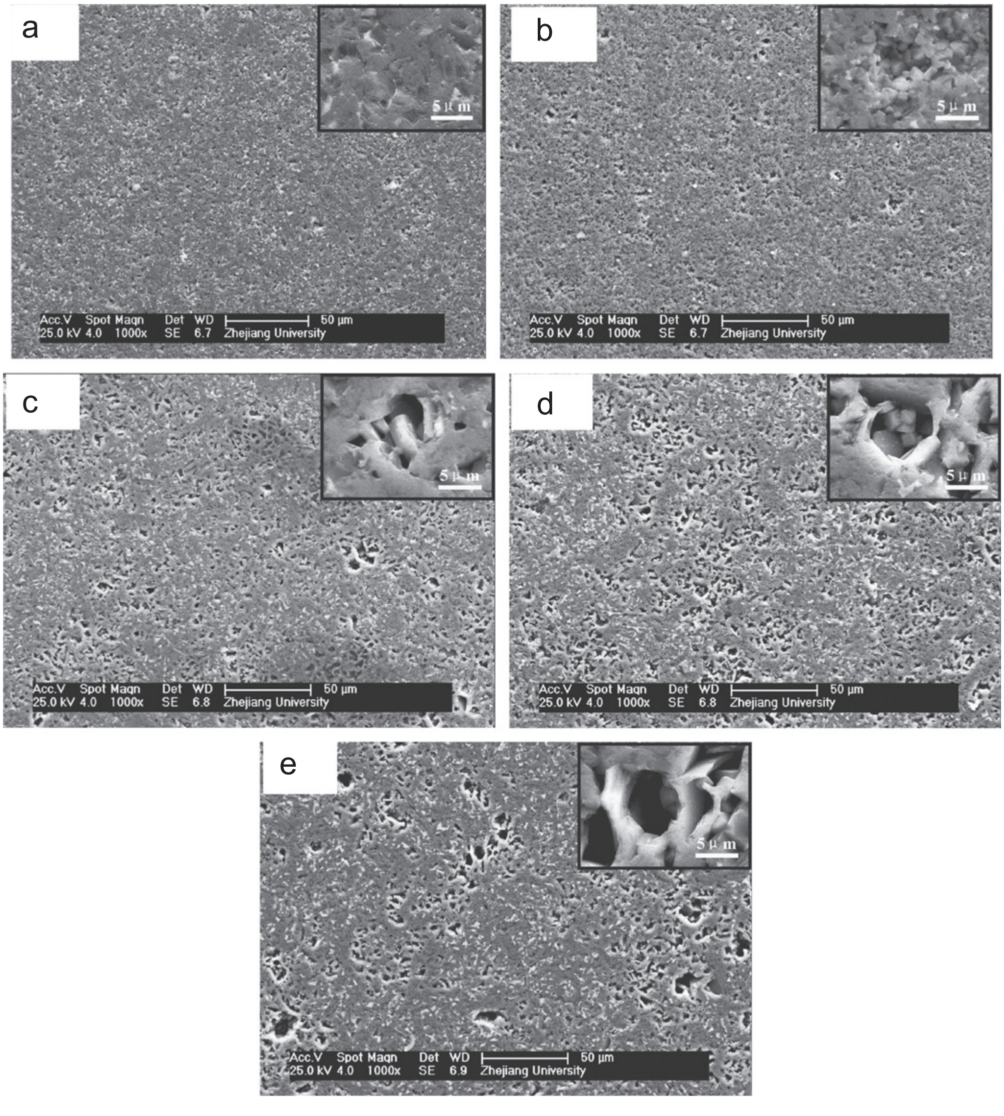

Fig. 3. SEM micrographs of polished section of LPS-SiC ceramic with different $CaCl_2$ contents. (a) 0 wt% $CaCl_2$; (b) 5 wt% $CaCl_2$; (c) 10 wt% $CaCl_2$; (d) 15 wt% $CaCl_2$ and (e) 20 wt% $CaCl_2$.

will produce a little volatilization at high sintering temperature. It is the reason why mass loss of SiC ceramic rapidly increases with the sintering temperature and $CaCl_2$ content. In addition, $CaCl_2$ particles in green bodies hinder the diffusion of material and weaken the sintering force during the sintering, which restricts the densification of SiC ceramics.

X-ray diffraction (XRD) patterns of SiC ceramics containing $CaCl_2$ are shown in Fig. 2. The major phases of sintered specimens are α-SiC (6H or 4H or 2H) and β-SiC (3C), with the existence of some YAG and CaCl2. YAG phase is presumably attributed to the reaction of Al_2O_3 and Y_2O_3 during sintering. $CaCl_2$ phase is attributed to the adding $CaCl_2$, which indicates that $CaCl_2$ phase does not react with other compositions and exists in the matrix individually.

It is also noted that the $CaCl_2$ phase changes a little with the increase of $CaCl_2$ contents, and has no effect on the main crystalline phases. It indicates that some $CaCl_2$ has volatilized during liquid phase sintering, but more $CaCl_2$ on the surface of the sintered body has resolved during machining and washing.

3.2. Investigation of surface and fracture microstructure

In this work, the formation of the pores mainly derived from the dissolving of $CaCl_2$ crystals. Therefore, controlling the size and shape of $CaCl_2$ crystals will determine the size and shape of the formed pores. SEM micrographs of finishing and fracture surfaces of LPS–SiC ceramics containing $CaCl_2$ after machining and washing with **de-ionized** water are shown in Figs. 3 and 4. From Fig. 3, it is seen that the polished surface of sintering sample containing no $CaCl_2$ (Fig. 3a) looks relative dense with some sintering defects. There are little open pores on the surface of the specimen with 5 wt% $CaCl_2$ (Fig. 3b), and the pores are small and

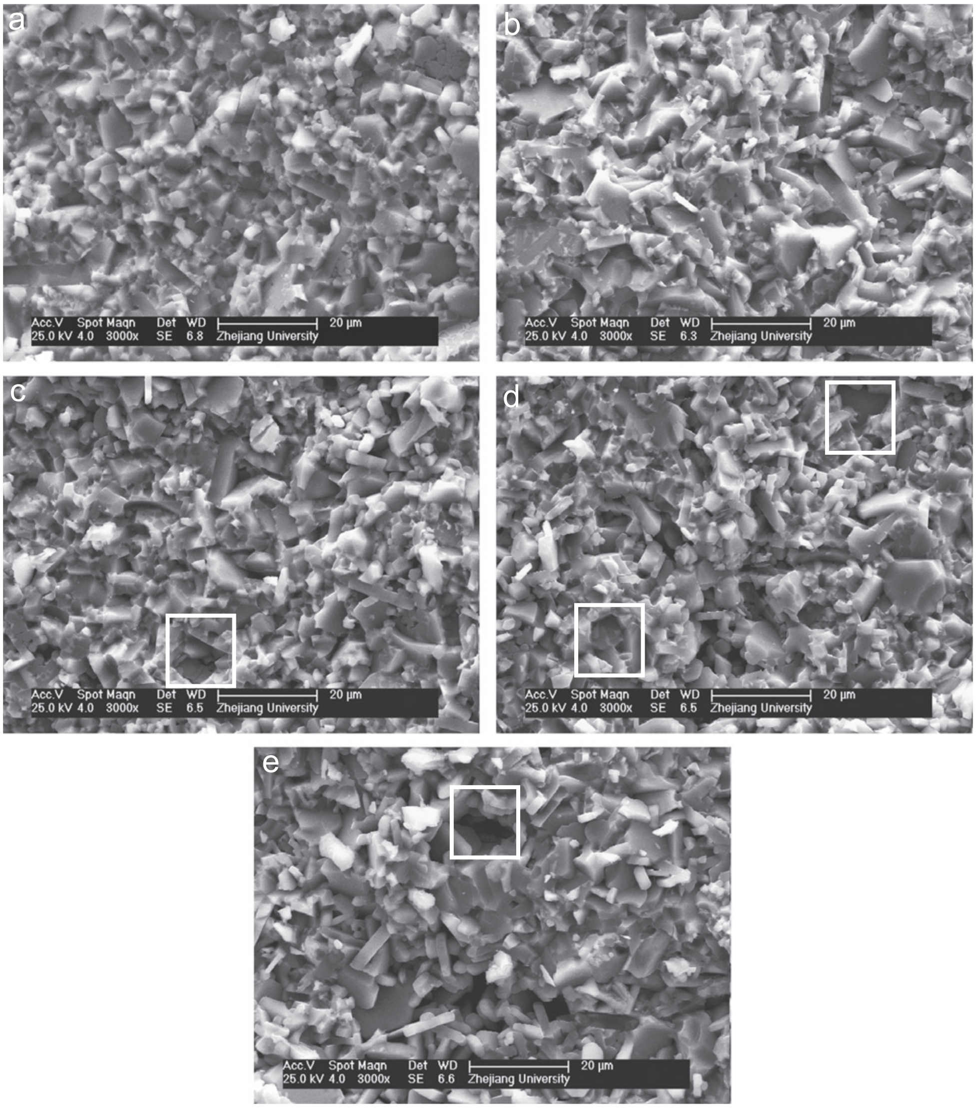

Fig. 4. SEM micrographs of fracture surface of LPS–SiC ceramic with different $CaCl_2$ contents. (a) 0 wt% $CaCl_2$; (b) 5 wt% $CaCl_2$; (c) 10 wt% $CaCl_2$; (d) 15 wt% $CaCl_2$ and (e) 20 wt% $CaCl_2$.

irregular. The number and size of pores obviously increase with the increase of $CaCl_2$, and the shape of pores becomes nearly circular (as upper right corner of Fig. 3c–e). However, there are some coherent and special larger pores in the sample with 20 wt% $CaCl_2$, implying the accumulation of $CaCl_2$ crystals during the sintering.

From Fig. 4, it is seen that the fracture surface of the samples without $CaCl_2$ looks very dense with no large pores, indicating high densification. With the increase of $CaCl_2$, the densification of fracture surface decreases and the combination of the crystals weakens, especially for the sample with 20 wt% $CaCl_2$, indicating weak interface bonding. It coordinates with the results of sintering behaviour (Fig. 1). There are some regular pores (white boxes) distributing on the fracture with the addition of more $CaCl_2$, which is possibly caused by the pulling out of $CaCl_2$ crystals.

The fractured mode of the composites with $CaCl_2$ is mainly intergranular fracture. The crystal size of the specimen slightly increases with the increase of $CaCl_2$. The crystal size of the sample containing no $CaCl_2$ is 1–2 μm, and increases to 3–5 μm at 20 wt% $CaCl_2$. It indicates that $CaCl_2$ particles cannot control the growth of SiC crystals. There are some $CaCl_2$ crystals distributing in the grain boundary of SiC. It proves that $CaCl_2$ crystals can accumulate on the surface and inside of the SiC ceramics, which is beneficial to achieve continuous pore-creation with the continued inwards of surface.

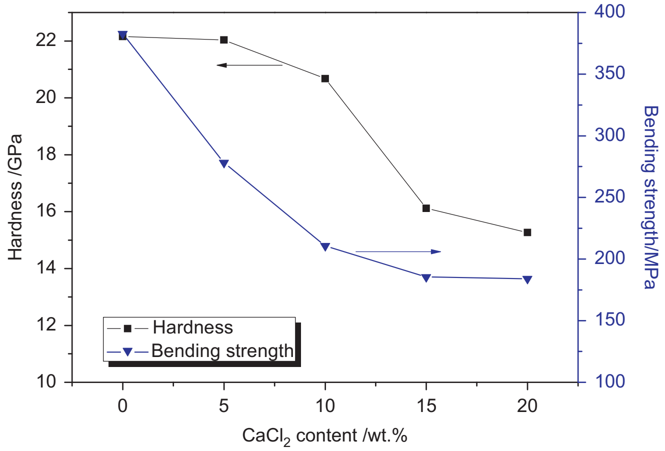

Fig. 5. Mechanical properties of LPS–SiC ceramics containing calcium chloride.

3.3. Investigation of mechanical and friction properties

Corresponding to SiC ceramics, the $CaCl_2$ is weak phase, and the formed pores are defect. It means that the addition of $CaCl_2$ and its pore-creation will inevitably worsen the mechanical properties. Fig. 5 shows the hardness and bending strength of LPS–SiC ceramic containing $CaCl_2$. It is noted that the bending strength and hardness decreased with the increase of $CaCl_2$ content. The hardness and bending strength of sintered sample without $CaCl_2$ are 22.16 GPa and 382.70 MPa, and reach to 15.26 GPa and 184.06 MPa at 20 wt% $CaCl_2$, respectively. It confirms that the addition of $CaCl_2$ lowers the mechanical properties of SiC ceramics.

According to the Chinese standard of mechanical seals (Specifications for silicon carbide rings of mechanical seal, JB/T 6374-2006), the bending strength of SiC sealing materials with graphite or pore-creation is required more than 150 MPa. It proves that all the bending strength in the experimental meet the requirement of Chinese standard. The mechanical properties of pore creating SiC ceramics by $CaCl_2$ are higher than those by volatilization of volatile pore-forming materials [15–21]. It confirms that $CaCl_2$ can improve the decrease extent of mechanical properties due to the addition of pore formers.

Fig. 6 shows dry friction coefficient of LPS–SiC ceramics containing calcium chloride. With the increase of $CaCl_2$ content, the dry friction coefficient of SiC ceramic obviously reduces. When the $CaCl_2$ content increases from 0 to 20 wt%, the dry friction coefficient rapidly decreases from 0.391 to 0.141, and the decrease extent is high, indicating an excellent friction property. Combined with the microstructure of SiC ceramics (Fig. 3), the dry friction coefficient directly depends on the open pores on the surface. The size of pores on the surface of SiC samples

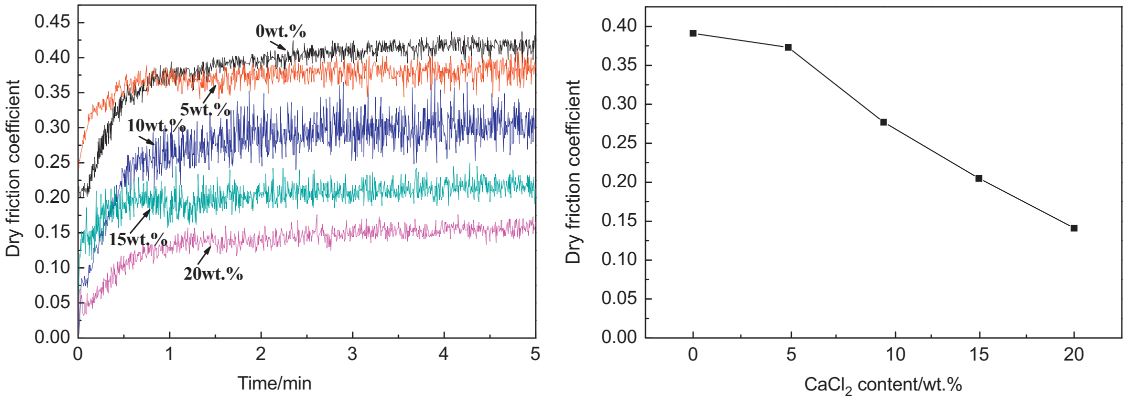

Fig. 6. Dry friction coefficient of LPS–SiC ceramics containing calcium chloride.

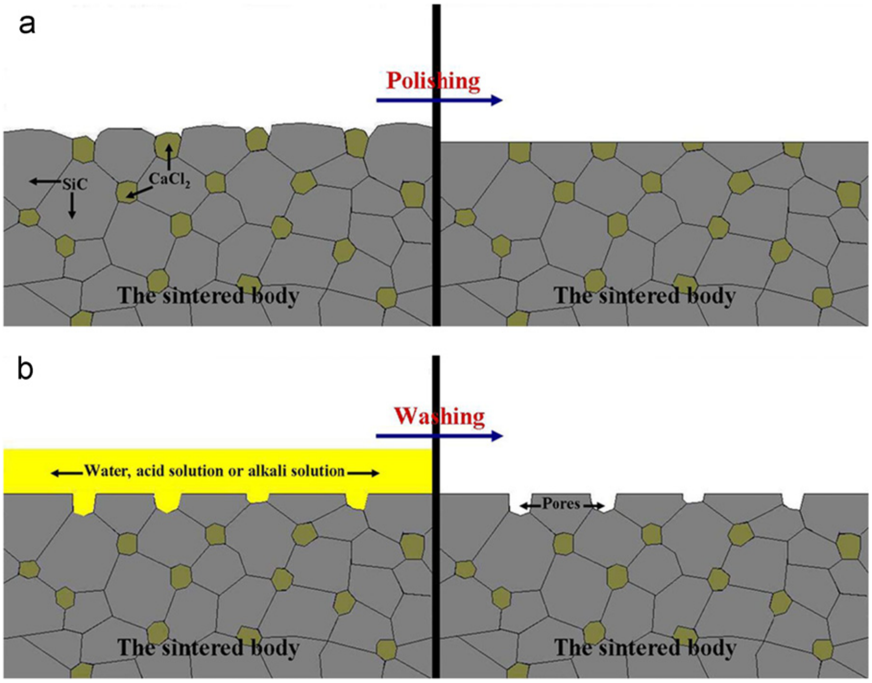

Fig. 7. Forming model of continuous pore-creating SiC ceramics with $CaCl_2$ during polishing (a) and washing (b).

increases with the $CaCl_2$ content, and the dry friction coefficient reduces accordingly. It confirms that the pore-creation is advantageous to reduce dry friction coefficient, and $CaCl_2$ can obviously improve the friction property of SiC ceramics.

4. Discussions

The formation model of continuous pore-creating SiC ceramics with $CaCl_2$ can be built, as shown in Fig. 7. In this system, the soluble $CaCl_2$ can firstly dissolve in SiC based aqueous slurry, and $CaCl_2$ particles form after spray-drying and uniformly disperse in the SiC granules. In the sintering, the $CaCl_2$ particles do not react with other compositions and participate in the sintering of SiC ceramic, while accumulate each other to form $CaCl_2$ crystals on the grain boundary of SiC ceramics. After polishing and washing, the surface porous SiC ceramics can be achieved because of the dissolving of surface calcium chloride crystals in water or acid or alkali washing medium.

During sealing, if the seal face with formed pores is exhausted, the seal face will extend to the inside of seals, which generates the new seal face with $CaCl_2$ crystals. When the new seal face meets water or other solvents, the $CaCl_2$ crystals will dissolve and create new pores. So, the continuous pore-creation will be achieved for SiC ceramics.

From above analysis and discussions, it is obtained that the addition of calcium chloride as pore former has two advantages: (1) continuous pore-creation on the surface and inside of SiC ceramics by its solubility and non-volatility; (2) reducing the friction coefficient of SiC ceramic.

5. Conclusions

SiC ceramics containing calcium chloride were prepared by liquid phase sintering. The $CaCl_2$ did not react with other compositions, and accumulatively formed $CaCl_2$ crystals on the grain boundary of SiC ceramics, which slightly restricted the growth of SiC crystals. The addition of $CaCl_2$ decreased the sintering and mechanical properties of SiC ceramic, but greatly reduced the friction coefficient. The pores on the surface and inside of SiC ceramics could be continuously created by the dissolving of $CaCl_2$ crystals. The addition of $CaCl_2$ was an effective pore former and improved the friction performances of SiC ceramics.

Acknowledgements

This work is supported by Innovation Fund for Technology-based Firms of China (12C26113303061), the High Science & Technique Brainstorm Project of Zhejiang Province of China (No. 2012C11112), Zhejiang Key Innovation Team Projects (No. 2009R50010), the Research Fund for the Doctoral Program of Higher Education (20070335017), and the Key Science & Technique Project of The Ministry of Education of China (109088).

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