Investigation on the formation of projections and cracks in anodic oxidation of reaction-sintered silicon carbide

Kang Peng1, Xinmin Shen1,3, Kazuya Yamamura2, Xiaonan Zhang1, Dong Wang1

1College of Field Engineering, PLA University of Science and Technology, No. 1 Haifu Street, Nanjing, Jiangsu 210007, China.
2Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.
E-mail: shenxmjflgdx2014@163.com

Abstract. Among the present oxidation-assisted polishing (OAP) technique, anodic oxidation is a promising method to process reaction-sintered silicon carbide (RS-SiC) with the assistance of abrasive polishing. Projections and cracks are inevitably formed in the anodic oxidation of RS-SiC for the volume expansion force. Evolvements of the oxide morphologies along with different oxidation voltage and different oxidation time are investigated by scanning electron microscope (SEM). It can be found that when the oxidation time stays the same, size of the projections and cracks on the oxidized RS-SiC sample is gradually enlarged. Meanwhile, when the oxidation voltage stays the same, size of the projections and cracks on the oxidized RS-SiC sample is also enlarged. Details of projections and cracks on the oxidized RS-SiC sample are obtained by the SEM with high magnification. Based on the theoretical derivation, it can be concluded that the formations of projections and cracks depend on the inner volume expansion force and the resultant force generated from other grains. Research on formation of projections and cracks in anodic oxidation of RS-SiC can promote the process level of RS-SiC products.

1. Introduction
Reaction-sintered silicon carbide (RS-SiC) has excellent mechanical and chemical properties, which makes it a novel and promising material for optics and ceramics [1, 2]. Many technologies have been developed to process RS-SiC, such as diamond lapping [3], plasma chemical vaporization machining [4], and so on. However, few of these techniques can obtain ultrasmooth surface, because there are SiC domains and Si domains in the RS-SiC substrates generated from the fabrication process. Along with the application of RS-SiC samples in the optical and ceramic fields, the requirements of surface quality of RS-SiC products are more and more strict. Oxidation-assisted polishing (OAP) is a novel method to process RS-SiC, which includes the oxidation of RS-SiC and the removal of oxide layer [5]. Many oxidation methods have been introduced to oxidize RS-SiC, such as the plasma oxidation [6, 7], thermal oxidation [8, 9], anodic oxidation [10, 11], and so on. Among these oxidation methods, anodic oxidation is a promising method to obtain high material removal rate (MRR) and the smooth surface quality simultaneously with the assistance of abrasive polishing by the ceria slurry [12, 13], because hardness of the oxide layer is remarkably smaller than that of the RS-SiC substrate [14, 15], and the anodic oxidation rate is larger than that in the thermal oxidation or that in the plasma oxidation [16-18].

Surface morphologies of the oxides determine the obtained surface quality of the RS-SiC sample with the assistance of abrasive polishing. Similar with other oxidation processes, the anodic oxidation
of RS-SiC sample is a volume expansion process, which indicates that the volume expansion force is inevitably generated [19-22]. The oxides generated from SiC/Si grains in the RS-SiC substrates extrude each other, which will result in complex oxide morphology. In this study, firstly, the oxide layer is generated by the anodic oxidation of RS-SiC in the mixture of hydrogen peroxide (H₂O₂) and hydrochloric acid (HCl). Secondly, the scanning electron microscope (SEM) is used to detect the oxidized RS-SiC sample, which can directly exhibit the oxide morphologies. Finally, a theoretical analysis on the formation of projections and cracks in anodic oxidation of RS-SiC is conducted, which is based on the oxidation processes of SiC grains and Si grains in the RS-SiC substrates.

2. Experimental apparatus and parameters

The anodic oxidation system applied in this study is shown in figure 1. The potential is supplied by the potentiostat, which is inspected by the sampling software in the controlling computer. The reference electrode (Ag/AgCl) is used to keep the oxidation potential constant by the feedback control. The electrical current is generated between the anode and cathode, and the oxide can be formed at the region of RS-SiC sample that contacts the electrolyte. The electrolyte used in this study is a mixture of the H₂O₂ and HCl, and their concentrations are 5.88wt% and 0.69wt%, respectively. In the oxidation system, H₂O₂ is treated as major oxidant, and HCl is used to increase conductance of the electrolyte.

![Figure 1. Schematic diagram of the used anodic oxidation system in this study.](image)

When the oxidation voltage is 9.8V and the oxidation time is 1800s, the obtained evolvement of the oxidation current along with the increasing of oxidation time is shown in figure 2, and the sampling time interval is 0.2s. Conductance of the RS-SiC sample is larger than that of the oxide layer. It can be found that the oxidation current can reach almost 240mA at the beginning, and it decreases rapidly along with the increasing of oxidation time, which indicates that the oxide layer is quickly formed in a short time. When the oxidation time arrives at 3.6s, the oxidation current falls down to 20mA. When the oxidation time increases from 3.6s to 100s, the oxidation current falls from 19.862mA to 1.128mA, which is close to the exponential decline. Along with the further increasing of the oxidation time, the reduction of oxidation current is smaller than 2µA when the oxidation time is increasing a sampling time interval 0.2s. Finally, when the oxidation time reaches 1800s, the oxidation current is 139.772µA, which is almost 1/1717 of the initial oxidation current 240mA. From the analysis on evolvement of the oxidation current, it can be found that the anodic oxidation rate of RS-SiC is decreasing along with the increasing of oxidation time, because the formed oxidation layer prevents the further oxidation process in the thickness direction. The maximum output of the potentiostat is 9.8V. Therefore, for the purpose of analyzing the formation of projections and cracks in anodic oxidation of RS-SiC, the experiments
are conducted in 12 series. In these experiments, the investigated oxidation potential is 2V to 9.8V, and the oxidation time is 10s to 3600s, as shown in Table 1.

![Graph showing oxidation current vs oxidation time](image)

**Figure 2.** Evolvement of the oxidation current along with the increasing of oxidation time.

**Table 1.** Experimental parameters in anodic oxidation of RS-SiC

| Serial number | Oxidation potential | Oxidation time | Oxidant                    |
|---------------|---------------------|----------------|----------------------------|
| 1             | 2V                  | 30s            |                            |
| 2             | 2V                  | 900s           |                            |
| 3             | 3V                  | 10s            |                            |
| 4             | 3V                  | 900s           |                            |
| 5             | 4V                  | 10s            |                            |
| 6             | 5V                  | 10s            | H₂O₂ (5.88wt%) and         |
|               |                     |                | HCl (0.69wt%)              |
| 7             | 5V                  | 900s           |                            |
| 8             | 7V                  | 10s            |                            |
| 9             | 7V                  | 900s           |                            |
| 10            | 9V                  | 10s            |                            |
| 11            | 9.8V                | 45s            |                            |
| 12            | 9.8V                | 3600s          |                            |

**3. Investigation on oxide morphologies**

Evolution of the oxide morphologies corresponding to the different oxidation voltages and different oxidation times are obtained by SEM, as shown in figure 3. It can be found that when the oxidation time stays the same, as shown in figures 3(a), 3(c), 3(e), 3(f), 3(h), and 3(j), size of the projections and cracks on the oxidized RS-SiC sample is gradually enlarged. Meanwhile, when the oxidation voltage stays the same, as shown in figures 3(a) and 3(b), or 3(c) and 3(d), or 3(f) and 3(g), or 3(h) and 3(i), or 3(k) and 3(l), size of the projections and cracks on the oxidized RS-SiC sample is also enlarged.
Figure 3. Evolutions of the oxide morphologies corresponding to the different oxidation voltage and different oxidation time.

(a) 2V and 30s. (b) 2V and 900s. (c) 3V and 10s. (d) 3V and 900s. (e) 4V and 10s. (f) 5V and 10s. (g) 5V and 900s. (h) 7V and 10s. (i) 7V and 900s. (j) 9V and 10s. (k) 9.8V and 45s. (l) 9.8V and 3600s.

Details of the projections and cracks on the oxidized RS-SiC sample are shown in figure 4. It can be found that most of projections are generated from initial SiC grains, and the oxides generated from Si grains have a relative smooth surface. From the figure 4(b) it can be found that there are cracks at the connecting regions among different SiC grains and Si grains, and width of the crack can be more than 50nm. Meanwhile, it can be judged from figure 4(c) that there is obvious crack on the formed projection, which is generated from the volume expansion force of the subsurface oxidized grains.
Figure 4. Details of projections and cracks on the oxidized RS-SiC sample obtained by SEM under high magnification.

(a) Projections. (b) Cracks. (c) Cracks on projection.

4. Study on oxidation mechanism

The major reason for formation of projection and crack is volume expansion of the oxidation process. The formulas for the anodic oxidation of the SiC grains and Si grains in the RS-SiC substrate can be summarized, as shown in formulas (1) and (2).

\[
\text{SiC} + 2H_2O \rightarrow \text{SiO}_2 + C + 2H_2 + O_2 \uparrow
\]

(1)

\[
\text{Si} + 2H_2O \rightarrow \text{SiO}_2 + 2H_2 + O_2 \uparrow
\]

(2)

The Molar mass \(M\) of SiC/Si/SiO\(_2\) is 40g/mol, 28g/mol, and 60g/mol, respectively, and the density \(\rho\) of SiC/Si/SiO\(_2\) is 3.22g/cm\(^3\), 2.32g/cm\(^3\), and 2.2g/cm\(^3\), respectively. From formulas (1) and (2) it can be found that the oxidation of SiC/Si to SiO\(_2\) is volume expansion process, and volume expansion coefficients of SiC and Si are 2.194 and 2.257, respectively. Supposing the volume expansion force from one grain is \(F\), and its direction is \((\alpha, \beta, \gamma)\) in the 3-dimensional systems. To a certain grain, supposing its serial number is \(k\), the inner volume expansion force generated from oxidation of itself is \(F_{\text{inner}}^k (\alpha_k, \beta_k, \gamma_k)\), as shown in equation (3), and the extrusion force generated from oxidation of other grains can be expressed by the equation (4).

\[
F_{\text{inner}}^k = F_k (\alpha_k, \beta_k, \gamma_k)
\]

(3)

\[
F_{\text{outer}} = \sum_{i=1}^{k-1} F_i (\alpha_i, \beta_i, \gamma_i) + \sum_{k+1}^{n} F_i (\alpha_i, \beta_i, \gamma_i)
\]

(4)

Therefore, when \(F_{\text{outer}} > F_{\text{inner}}\), projections are formed, as shown in the figure 4(a). Otherwise, if \(F_{\text{outer}} < F_{\text{inner}}\), cracks are produced, as shown in figure 4(b). What’s more, the volume expansion force generated from oxidation of the subsurface grains can result in crack on the projection, as shown in the figure 4(c). The volume expansion force \(F\) is determined by the oxidation potential and the oxidation time. The exact value of \(F\) can be obtained in the finite element analysis (FEA) by simulating the oxidation process, which is the direction of the further research. Characters of the oxide morphologies affect the obtained MRR and surface quality in the following abrasive polishing process. On the one hand, the hardness of the oxide is obviously lower than that of the initial RS-SiC substrates, and the projections and cracks on the soft oxides increase the contact areas with ceria particles in the abrasive polishing process; thus, high MRR can be easily obtained in anodically oxidation-assisted polishing (AOAP) of RS-SiC. On the other hand, some cracks penetrate into the oxidized RS-SiC sample, which is very difficult to remove completely with the assistance of abrasive polishing; thus, it is difficult to obtain an ultrasmooth surface in the AOAP of RS-SiC. Therefore, AOAP can be treated as an efficient method for the rapid figuring of RS-SiC, which can improve the process level of the RS-SiC sample.
5. Conclusions

Projections and cracks are generated in the anodic oxidation of RS-SiC for the volume expansion force. For the oxide generated from a certain grain, if the inner volume expansion force is smaller than the resultant force generated from other grains, projections are formed. Otherwise, cracks can be produced. Since the oxidation current pass through all the RS-SiC, the volume expansion force generated from the oxidation of subsurface grains can press surface oxide to result in cracks on the projection.

Characters of the oxide morphologies affect the obtained MRR and surface quality in the following abrasive polishing process. AOAP of RS-SiC can obtain high MRR and relatively fine surface quality. Therefore, AOAP can be treated as an efficient method for the rapid figuring of RS-SiC, which can improve the process level of the RS-SiC sample and promote the application of RS-SiC products.

This work was supported by a grant from National Natural Science Foundation of China (Grant No. 51505498) and a grant from Natural Science Foundation of Jiangsu Province (Grant No. BK20150714). The authors also express their gratitude to the staffs and students of Research Center for Ultra-precision Science and Technology of Osaka University.

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