Investigations on the oxidation phenomenon of SiC/SiC fabricated by high repetition frequency femtosecond laser

Zhaoyang Zhai [a], *, Chen Wei [a], Yanchao Zhang [a], Yahui Cui [a], Quanren Zeng [b]

[a] *School of Mechanical and Precision Instrument Engineering, Xi'an University of Technology, Xi'an, China;*

[b] *Department of Design, Manufacture and Engineering Management, University of Strathclyde, Glasgow, UK.*

Abstract: SiC/SiC was processed by high repetition frequency femtosecond laser with a wavelength of 1030 nm. The experimental results were analyzed based on the finite element simulation. In the femtosecond laser ablation experiment of SiC/SiC, the processing morphologies under different laser power, repetition frequency, scanning times and scanning velocity were compared. It was found that surface oxidation is an obvious defect in the high-frequency femtosecond laser processing of SiC/SiC, which needs to be controlled. The oxidation phenomenon became more and more obvious with the increased of laser power, repetition frequency and scanning times, while it decreased with the increased of scanning velocity. The parameters of material and laser processing were input into the heat transfer module of the finite element simulation software. The simulation results could intuitively show the formation of different morphological features from the perspective of the temperature field. Finally, the surface oxidation of SiC/SiC was effectively controlled through rationally optimizing the laser processing parameters, and good morphology was obtained. The comparison between simulation and experimental results can help to understand the ablation mechanism of SiC/SiC by high-frequency femtosecond laser, and provide reference for the efficient and precise manufacture of CMC-SiC materials by pulsed laser.

Keywords: High repetition frequency femtosecond laser; SiC/SiC; Surface oxidation; Heat transfer simulation

1 Introduction

As aerospace science and technology changes rapidly, aerospace manufacturing industry is increasingly demanding the performance of materials [1]. Researchers in various countries are placing more and more attention on the new high-performance materials and advanced composite materials for the versatility, structural integrity and design flexibility [2]. Silicon Carbide Ceramic Matrix Composites (CMC-SiC) are featured by low density, high strength, high temperature resistance and corrosion resistance [3], and the reinforcement and toughening effect of the fiber inside the material effectively overcomes the shortcomings of poor fracture toughness of the ceramic material, making this new composite material be widely used in the aerospace field and

* Corresponding author.
E-mail address: zyzhai@xaut.edu.cn (Z.Y. Zhai)

become the development trend of material selection of hot components. CMC-SiC is mainly divided into two types based on the internal fiber composition, namely Carbon Fiber Reinforced Silicon Carbide (C/SiC) and Silicon Carbide Fiber Reinforced Silicon Carbide (SiC/SiC) [4, 5]. The density of CMC-SiC material is only 30% of that of high-temperature alloy, and the operating temperature is higher than that of superalloy by more than 200 K without air cooling and thermal barrier coating. The CMC-SiC components used in aero engines can reduce the weight and the amount of cooling air, improve the inlet temperature and efficiency of the turbine, and reduce the fuel loss and consumption. However, the processed functionalized structure of the material needs to meet the required accuracy to assemble CMC-SiC components into aerospace vehicles [6].

CMC-SiC is difficult-to-machining material with ultra-high hardness. Especially, in the traditional mechanical cutting, the anisotropic CMC-SiC materials are easy to produce burrs, delamination, tearing and chipping in the processing region due to the cutting force [7]. These processing defects directly affect the processing quality and even lead to the scrapping of the parts. The special processing technology differs from traditional processing methods and belongs to non-contact processing. The special processing technology successfully applied to CMC-SiC materials includes water jet machining, ultrasonic processing, electric discharge machining and laser processing [8]. Water jet machining tends to produce fiber pullout on the surface of the material during processing. The accuracy of ultrasonic machining is limited by the amplitude. The recasting layer of electrical discharge machining is obvious. These processes are not qualified for the processing of CMC-SiC materials. Among these processing processes, laser processing has obvious advantages, including high processing quality, non-contact processing, low heat input to materials, and wide application range, and is easy to integrate with numerical control technology to achieve automation [9]. From the perspective of the development of aero engine manufacturing technology, pulsed laser processing will become the mainstream technology for the preparation of surface microstructure of CMC-SiC components in the future [10].

In order to complete high-efficiency processing of large removal in a short time, high-power and long-pulse lasers were used in laser ablation research of CMC-SiC [11]. Liu et al. [12] carried out experimental researches on the thermo-mechanical response of continuous laser irradiated carbon fiber reinforced composites. They found that due to the influence of thermal stress concentration in the laser processing, there was obvious interface delimitation. Because CMC-SiC is woven with multi-layer fibers, it will produce defects in pulsed laser processing, which are different from that of homogeneous materials. Wu et al. [13] conducted ablation experiments on C/SiC with pulsed laser in the direction perpendicular to, parallel to, and axes of fibers, respectively. The results showed that, under the premise of the same processing parameters, the size of the obtained microstructure morphology varied with the scanning direction, and there were processing defects, such as fiber breakage, matrix loss, and microcrack, in the microstructure generated by laser ablation. In the laser ablation process of CMC-SiC materials, because SiC is the main component of CMC-SiC, and it will generate SiO_2 due to the thermal effect caused by the accumulation of laser pulses, which will cause surface oxidation of the material. Wang et al. [14] processed the C/SiC materials with pulsed laser in the air environment. They found that the bottom, side walls and edges of the processing region were covered with white particles. In recent years, scholars focused the precision machining of CMC-SiC by ultrashort pulse laser to suppress the processing defects caused by thermal action on CMC-SiC materials. Wang et al. [15] conducted research on the micro-machining process and mechanism of C/SiC by picosecond laser. Moreno et al. [16] conducted experimental studies on the carbon reinforced materials, which were processed by femtosecond laser. It was found that, under the control of laser parameters, fiber reinforced composites could obtain better processing quality by ultrashort pulse laser due to its short pulse duration and high peak power density.

Since CMC-SiC materials are widely used in the aerospace field and become the development trend of material selection of hot components, now the researches on laser processing of CMC-SiC are still in the initial stage. Most of researches focus on the influence of various laser parameters on the processing effect of CMC-SiC. The causes and improvement methods of processing defects are still unclear, and it is impossible to realize the laser processing of high-quality functional microstructure of CMC-SiC. Surface oxidation [17, 18] is an obvious defect in the laser processing of CMC-SiC, which needs to be controlled. Because the researchers have found that water vapor in the atmosphere reacted with SiO_2 which can generate $Si(OH)_4$ on the surface of CMC-SiC material at high temperature. The properties of CMC-SiC materials will degrade with the continuous reaction. Ultimately, it will lead to damage and failure of CMC-SiC components in the critical condition. Therefore, it is necessary to further research the ablation mechanism of the pulsed laser on the surface microstructure of the material, accurately grasp the formation conditions and evolution mechanism of the surface microstructure, and finally realize the efficient and precise manufacturing of the CMC-SiC material by pulsed laser on a large scale.

2 Experimental method

The performance of CMC-SiC is closely related to its preparation process. The current mainstream preparation processes in the industry are Precursor Infiltration Pyrolysis (PIP), Chemical Vapor Infiltration (CVI), and Melt Infiltration (MI). The surface and internal morphology of CMC-SiC prepared by different processes are quite different. The SiC/SiC sheets used in the experiment were prepared by the MI process, the components prepared by which are relatively compact, with small amount of processing deformation, making it easier to achieve near net shaping. SiC/SiC consists mainly of the outermost SiC deposition layer, the inner SiC matrix, the SiC fiber, and the pyrolytic carbon (PyC) interfacial layer, and there are many tiny pores in the SiC fiber woven structure. The morphology of the experiment material is shown in Fig. 1, and its performance characteristic parameters are shown in Table 1.

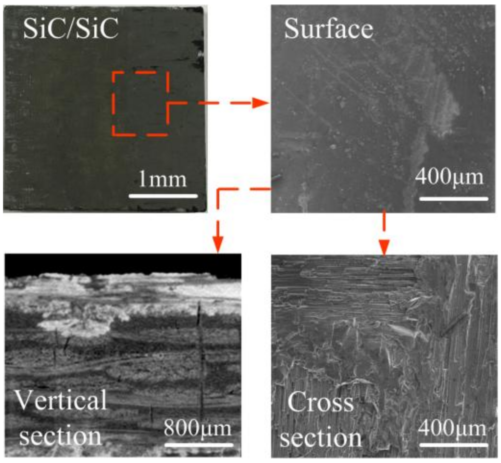

Fig. 1. SiC/SiC surface morphology.

Table 1 Table of material characteristics.

Parameter	Value
Diameter of carbon fiber	12 μm
Thickness of PyC layer	0.2 μm
Density	2.8 g/cm^3
Fiber volume fraction	60 %
Porosity	5 %
Size	30×30×5 mm^3

The Pharos 20 W Yb: KGW all-solid-state femtosecond laser used in the experiment was produced by Light Conversion. The output power, repetition frequency, pulse width and single pulse energy of the femtosecond laser can be directly adjusted through software. The morphology was observed through Hitachi SU8010 field emission scanning electron microscope (FESEM). The specific dimensions were measured by the OLS4000 laser confocal microscope manufactured by Olympus. The Raman scattering spectra of different samples were collected using a Horiba HR800 Raman microscope. The Cambridge Technology EC1000 laser scanning galvanometer system with a JENar 170-1030 F-theta lens was applied in the femtosecond laser processing of SiC/SiC. The experimental light paths are shown in Fig. 2. The processing parameters are presented in Table 2.

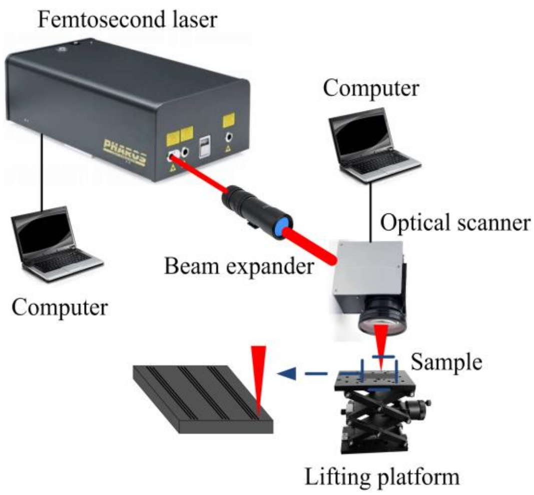

Fig. 2. Light paths in the experiment.

Table 2 Table of processing parameters.

Parameter	Value
Wavelength	1030 nm
Maximum power	20 W
Pulse width	290 fs
Maximum single pulse energy	0.2 mJ
Repetition frequency	1 Hz~200 kHz
Laser mode	TEM_{00} (M^2<1.3)

3 Results and discussion

3.1 Experimental results

A series of femtosecond laser processing experiments was carried out under different parameters to study the processing effect of SiC/SiC surface in detail. Laser wavelength [19, 20] determines the characteristic size of microgroove by affecting the spot size, Rayleigh length and the absorption rate of laser energy. The pulse width of laser has an important influence on the scale and morphology characteristics of laser ablation. In order to focus on the oxidation phenomenon of SiC/SiC fabricated by high repetition frequency femtosecond laser, the main parameters changed in this study include laser power, repetition frequency, scanning times and scanning velocity. The processing effect is shown in Fig. 3. It can be seen from the figure that there was a white oxide accumulation at the edge of the SiC/SiC surface processed by femtosecond laser. Since SiC is the main component constituting CMC-SiC, it will generate SiO_2 due to the thermal effect caused by the accumulation of laser pulses, which will cause surface oxidation of the material. The oxidation phenomenon gradually became pronounced with the increase of laser power, repetition frequency and scanning times, but as the scanning velocity increased, the oxidation phenomenon gradually decreased. When the working state of the laser and the scanning galvanometer was stable, it was found that the processing quality of the SiC/SiC surface processed by high-frequency femtosecond laser was not ideal.

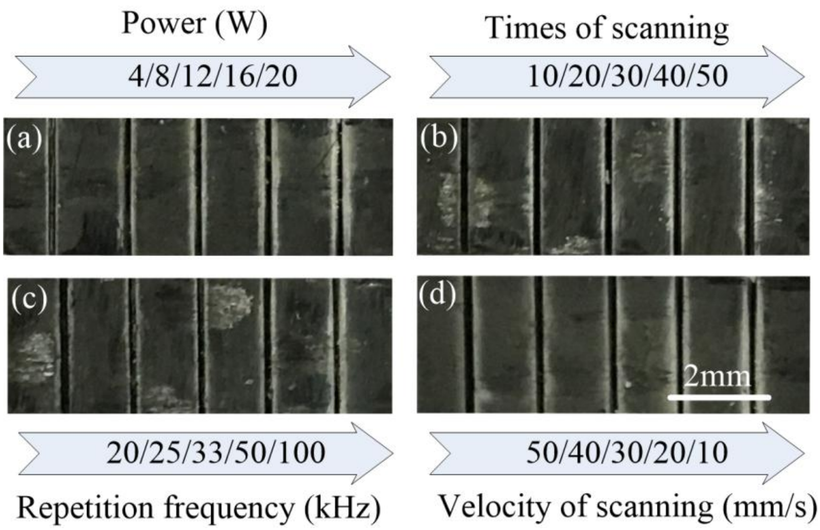

Fig. 3. Surface morphology of SiC/SiC processed by femtosecond laser with different parameters: (a) power, (b) times of scanning, (c) repetition frequency, (d) velocity of scanning.

Surface oxidation is a processing defect which needs to be controlled in the high-frequency femtosecond laser processing of SiC/SiC. The SEM was used to observe the ablation region of femtosecond laser on the SiC/SiC surface, as shown in Fig. 4. After processed by the high-frequency femtosecond laser, there was a large amount of debris at the edge of the processing region, and the debris constantly gathered on the surface with the increase of laser power, repetition frequency, and scanning times. The variation law of the processing morphology with the change of power was taken as an example. When the processing power was 4 W, the debris was dispersed and arranged in granular form; as the power increased, the particles gradually changed into floccule; and when the processing power increased to 20 W, that the dispersed floccule gradually agglomerated, and that the debris accumulated on the surface and gathered continuously under the effect of heat. The reasons for forming the morphology are as follows. First, under the irradiation of low power laser, the material absorbs the laser energy, and the amount of debris formed is small, which is completely dispersed. Second, when the processing power gradually increases, the laser energy increases accordingly, and the amount of debris formed by the absorbing the laser energy significantly increases, the debris is gradually changed from granular form to floccule. Last, as the laser energy further increases, the debris in the dispersed state increases, continuously gathers under the action of thermal effect, and continuously accumulates at the edge of the processing region. The change rule of processing morphology with repetition frequency, scanning times and scanning velocity was similar with it.

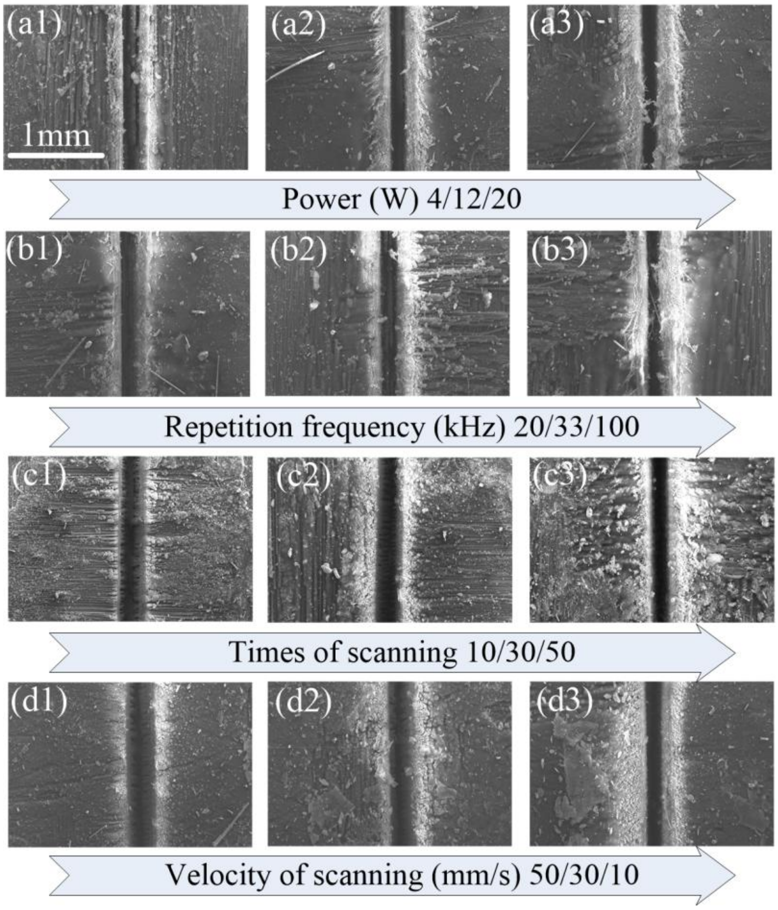

Fig. 4. Surface morphology of SiC/SiC processed by femtosecond laser with different parameters: (a) power, (b) times of scanning, (c) repetition frequency, (d) velocity of scanning.

SiC/SiC was cleaned in an ultrasonic cleaner with alcohol to clearly observe the ablation region, the surface morphology of the cleaned SiC/SiC and the energy dispersion spectrum (EDS) analysis are shown in Fig. 5. It can be seen that the debris adhering to the SiC/SiC surface was removed by ultrasonic cleaning, and that the oxide at the edge of the processing region was still deposited on the SiC/SiC surface after ultrasonic cleaning due to its compact structure. At the edge of the processing region, the material reacted chemically with oxygen in the air after absorbing laser pulse energy, as shown in Eqs. (1), (2) and (3) [21, 22]. Since the laser processing was carried out in the air, it will generate air plasma, which contains O that is easy to combine with positive ions. The content of O combined with positive ions is low in the low-power femtosecond laser processing, and Si and C do not fully combine with oxygen, producing oxides of C and Si. The gaseous products CO and CO_2 will volatilize with the gas stream, but the oxide of Si will adhere to the surface in the form of debris, of which the composition is mainly SiO_2.

$$2O_2(g)+SiC(s)=SiO_2(s)+CO_2(g) \tag{1}$$

$$3O_2(g)+2SiC(s)=2SiO_2(s)+2CO(g) \tag{2}$$

$$O_2(g)+SiC(s)=SiO(g)+CO(g) \tag{3}$$

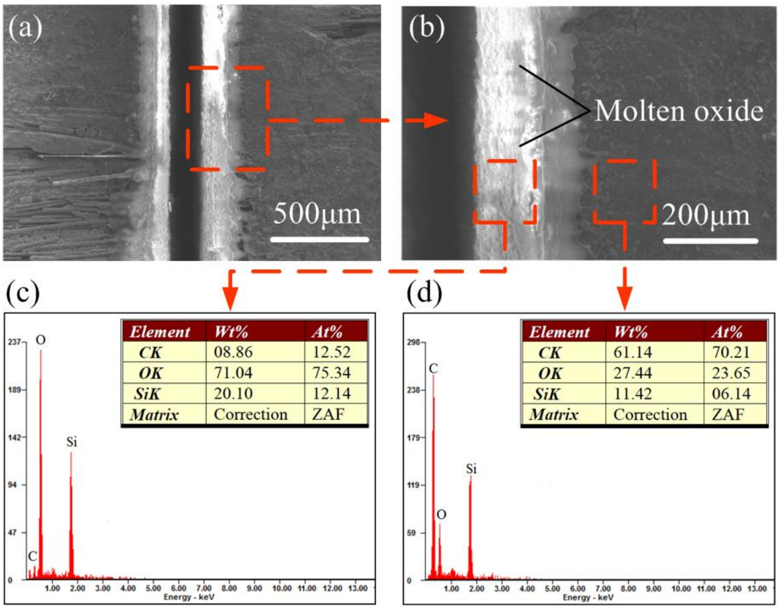

Fig. 5. Surface morphology of SiC/SiC processed by femtosecond laser: (a) low-magnification, (b) high-magnification, (c) EDS analysis of oxide layer, (d) EDS analysis of unmachined surface.

Fig. 6 is the analysis of Raman spectrum before and after processing of SiC/SiC surface. The SiC crystal structure on SiC/SiC surface was 3C-SiC. The area of Raman spectrum showed that, after the femtosecond laser processing, SiC content was reduced, while the relative content of SiO_2 was increased. The existence of D band and G band of SiC/SiC surface were observed in the Raman spectrum, which suggested that, the C of SiC/SiC surface had structure similar with amorphous carbon. This kind of structure displayed certain disorderliness. After femtosecond laser processing, the degree of graphitization was increased.

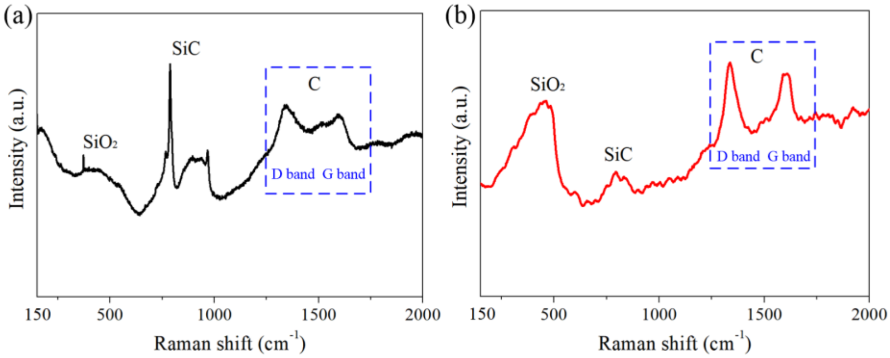

Fig. 6. Raman spectra of the SiC/SiC surface: (a) unmachined surface, (b) oxide layer.

The oxide layer width of the ablation region on the SiC/SiC surface varied with processing parameters, and the curve of variation is shown in Fig. 7. It can be seen that, for surface processing, the laser power is critical to the change in surface morphology and composition after processing. High-power femtosecond laser processing will produce a lot of debris, which will result in a greater damage to the surface morphology and more serious oxidation. Therefore, low-power femtosecond laser is suitable for the surface processing. It can achieve small damage and improve the processing quality while completing the surface processing requirements. The repetition frequency and scanning velocity directly determine the overlapping rate of the laser spot, as shown in Eq. (4). Based on the experimental results, it was found that the overlapping rate of laser spot has a great effect on the processing quality of femtosecond laser. During processing, the removal of materials is mainly due to the accumulation of a large number of pulses. When the overlapping rate of laser spot decreases, the number of effective pulses affecting the material decreases, and therefore, it will directly affect the ablation depth. However, with the increase of the overlapping rate of laser spot, the distance between adjacent pulses decreases, and more heat is accumulated per unit area, which results in an increase in the thickness of the oxide layer. The distribution of laser energy is not directly related to the number of pulses, therefore, the change of the overlapping rate of laser spot does not impact the processing width. In large-scale processing of materials, a large amount of material removal is usually obtained through increasing the laser scanning times.

$$\delta = \left(1 - \frac{v}{D_0 f}\right) \times 100\% \tag{4}$$

In this expression, D_0 is the laser spot diameter at the focal plane, v is the scanning velocity, f is the repetition frequency.

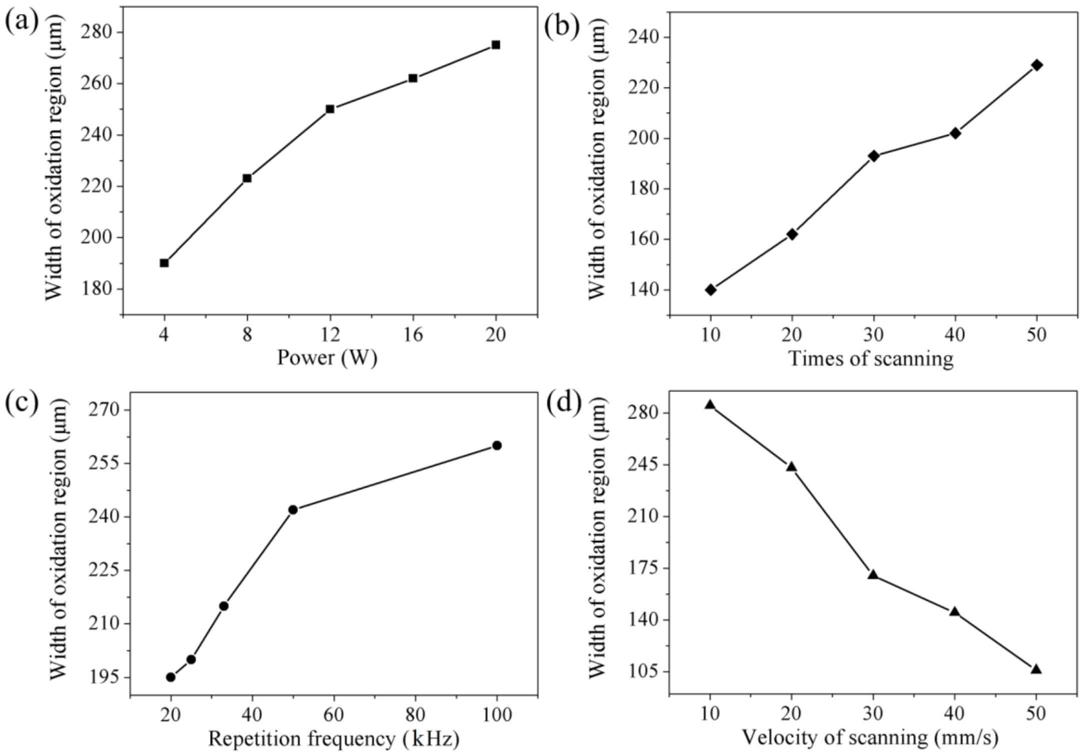

Fig. 7. Oxide layer width of the ablation region on the SiC/SiC surface with different parameters: (a) power, (b) times of scanning, (c) repetition frequency, (d) velocity of scanning.

High-power femtosecond laser processing will produce a lot of debris, which will result in a greater damage to the surface morphology and more serious oxidation. Therefore, low-power femtosecond laser is suitable for the surface processing. It can achieve small damage and improve the processing quality while completing the surface processing requirements. Compared with the high-power femtosecond laser, the low-power femtosecond laser with a processing power of 2 W (16 J/cm^2, 10 kHz, 50 mm/s) ablated on the SiC/SiC surface with less residual debris, making it more suitable for the SiC/SiC surface processing. The processing morphology is shown in Fig. 8. There was still a small amount of oxide accumulated at the edge of the SiC/SiC surface processing region.

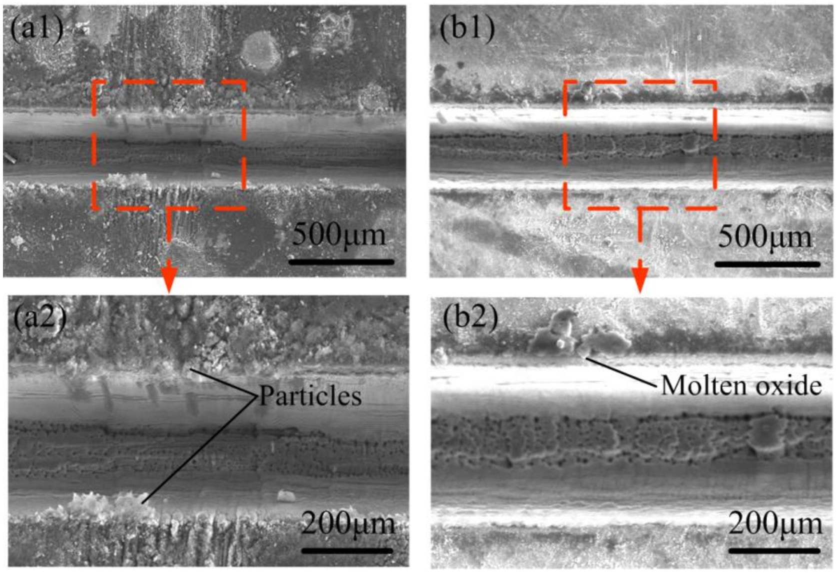

Fig. 8. Surface morphology of SiC/SiC processed by femtosecond laser: (a) uncleaned, (b) cleaned.

In order to further control the surface oxidation of SiC/SiC and obtain better morphology quality, the overlapping rate of laser spot was controlled and the distance between adjacent pulses was reduced by adjusting the repetition frequency and scanning velocity of the laser, thereby reducing the heat accumulation in the unit area during laser processing. Fig. 9 shows the SiC/SiC morphology processed under different scanning interval. It was found that the surface oxidation of SiC/SiC was effectively controlled, and that no oxide accumulation occured at the edge of the processing region, good morphology quality was obtained. Calculated results showed that the overlapping rate of laser spot was 75% (2 W, 16 J/cm^2, 10 kHz, 100 mm/s).

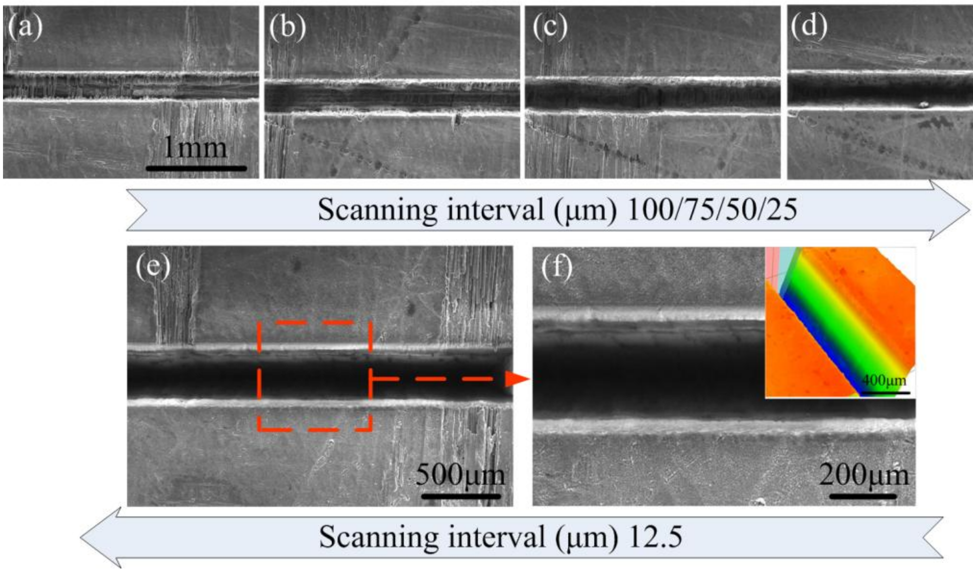

Fig. 9. Surface morphology of SiC/SiC processed by femtosecond laser with different scanning interval: (a) 100 μm, (b) 75 μm, (c) 50 μm, (d) 25 μm, (e) 12.5 μm, (f) high-magnification.

It should be noted that, in the laser processing of SiC/SiC, better quality could not be obtained with lower overlapping rate of laser spot. Lower overlapping rate of laser spot will result in a decrease of the number of effective pulses acting on the material. It directly affects the ablation depth and the morphology in the ablation region. The processing morphology is shown in Fig. 10. Lower overlapping rate of laser spot will result in uneven laser energy received at the surface of the material, and even separation between the spots, leading to different material removal amount. Therefore, the edges and sidewalls of the processing region are serrated, and this morphology is more pronounced as the overlapping rate of laser spot decreases.

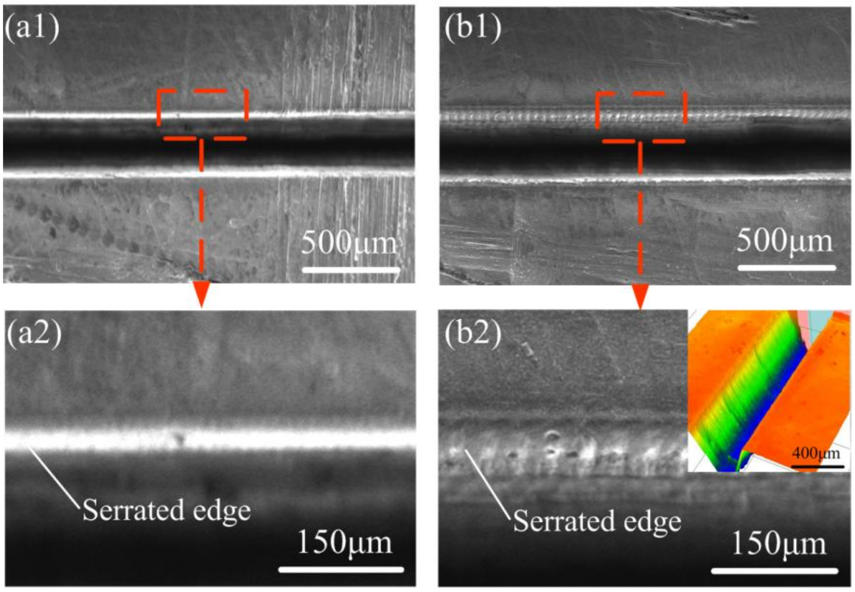

Fig. 10. Surface morphology of SiC/SiC processed by femtosecond laser with different scanning velocity: (a) 150 mm/s, (b) 200 mm/s.

In addition, because linear polarized beam was used in the experiment, waviness features can be observed in a magnified SEM micrograph in the part of the bottom and wall of processing region, as shown in Fig. 11. These waviness features are generally described as ripples or laser induced periodic surface structures [23, 24] for other materials. A feasible way to avoid the formation of surface ripples is to convert the linear polarization state of laser into circular polarization state through the use of a 1/4 wave plate in the light paths.

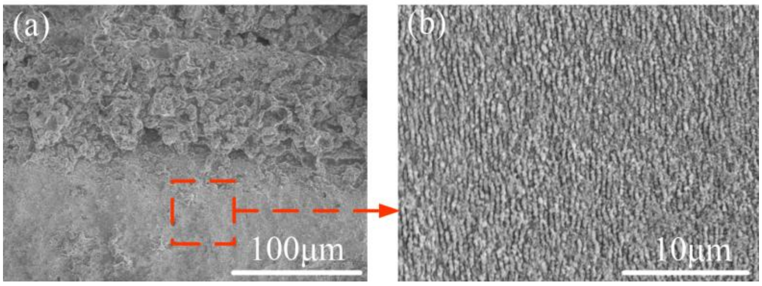

Fig. 11. Laser induced periodic surface structures: (a) low-magnification, (b) high-magnification.

The material removal induced by a femtosecond laser is a complicated physicochemical process, accompanied by the absorption of laser energy, thermal conduction, avalanche ionization, plasma expansion, liquid phase blasting, and other processes. SiC [25] has a 3.02 eV band gap and the photon energy of a laser pulse at 1030 nm is 1.2 eV, so ionization will be achieved only through multi-photon non-linear absorption. Ionization of SiC takes place after absorbing the multi-photon energy, and the number of free electrons will increase by great leaps due to the avalanche effect to produce plasma. The femtosecond laser has a short pulse width, so the influence of plasma shielding can be effectively avoided. Because the action time of femtosecond laser is much smaller than the lattice relaxation time, the thermal energy converted from photon energy after absorbed by SiC can only be conducted inside the crystal lattice, and has little thermal effect on the surrounding materials. However, in practical applications, it can be found from the experimental results that femtosecond laser processing also has a thermal effect on the surrounding materials due to the existence of pulse accumulation effect. The ablation principle of the femtosecond laser on the SiC/SiC surface is shown in Fig. 12. From the perspective of laser energy, the ablation rate of SiC/SiC by femtosecond laser is composed of two parts, namely photochemical ablation rate and photothermal ablation rate. When the high-frequency femtosecond laser irradiates the surface of SiC/SiC, photothermal action and photochemical action simultaneously act on the material. When the laser energy and the overlapping ratio of laser spot are small, the interval between pulses is smaller than the thermal relaxation time, and the photochemical action is dominant. As the laser energy and the overlapping ratio of laser spot increase, the photothermal effect gradually dominate. In general, this thermal effect is disadvantageous in femtosecond laser processing, which will lead to the decline in processing accuracy and surface quality.

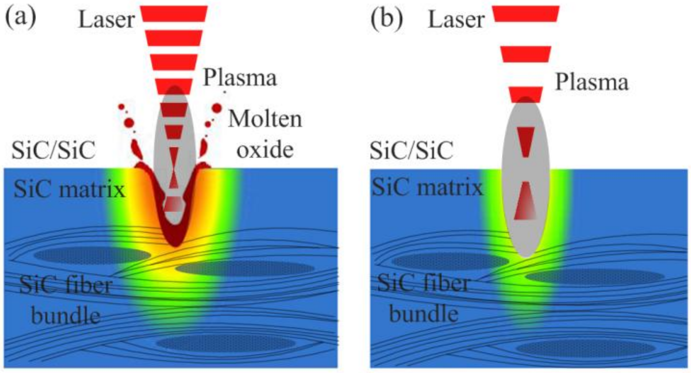

Fig. 12. Schematic diagrams of ablation mechanisms: (a) photothermal effect, (b) photochemical effect.

In the SiC/SiC surface processing of femtosecond laser, when the laser energy and the overlapping ratio of laser spot are large, the photothermal action will make the material melt, and the flying molten matter will disperse and shrink into particulates due to surface tension, thus forming the observed sparking phenomenon. The accumulated heat per unit area can be reduced by adjusting the laser power and the overlapping rate of laser spot. Under action of photochemistry, SiC/SiC ionizes after absorbing multiphoton energy and forms plasma. The ablation process of femtosecond laser on the SiC/SiC surface is shown in Fig. 13.

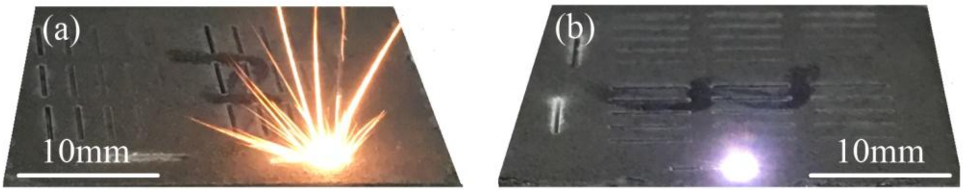

Fig. 13. Ablation process of femtosecond laser on the SiC/SiC surface: (a) photothermal effect, (b) photochemical effect.

3.2 Theoretical analysis and verification

High-frequency and high laser power are conducive to improving the processing efficiency, but at the same time bring new problems. When the overlapping ratio of the laser pulses is too large, the heat accumulation between the pulses becomes more and more significant. In general, this thermal effect is disadvantageous in femtosecond laser processing, which will lead to the reduction in processing accuracy and surface quality. Researchers can use the complex geometric models in the heat transfer modules of COMSOL Multiphysics to study the effects of heating and cooling processes on materials. This module can simulate the heat transfer mechanisms of materials, including conduction, convection, and radiation. The heat transfer simulation can be performed in three-dimensional coordinate systems to solve the steady and transient problems. The specific solution steps in this study are as follows: constructing a two-dimensional geometric model of the SiC layer on the SiC/SiC surface; defining the properties of the SiC material, and selecting solid heat transfer as the analysis type; defining the boundary conditions and initial values based on the laser processing parameters; setting the laser source to move along the scanning direction at a constant velocity; applying the laser heat source load to the SiC layer of the SiC/SiC surface in the type of heat flow density. The simulation model is shown in Fig. 14. The geometric model was meshed, and the transient solver was selected for calculation, and finally the results were visualized. In the simulation model, the part of laser energy used for thermal effect was controlled by a coefficient.

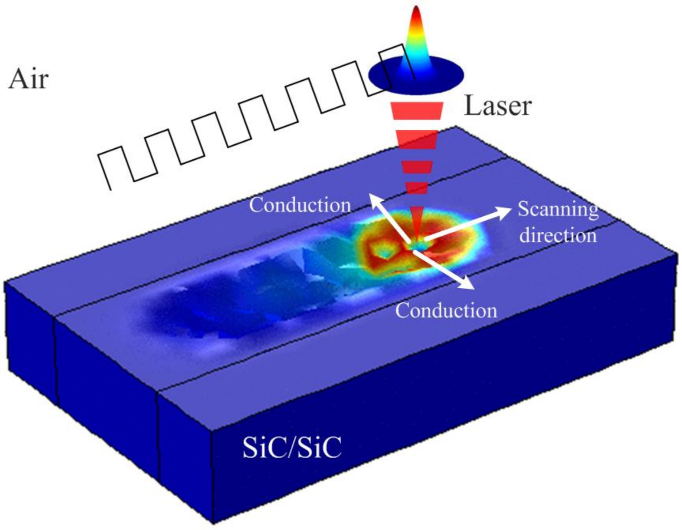

Fig. 14. Model of laser processing simulation of SiC/SiC.

Fig. 15 shows the surface temperature distribution and isotherm of SiC/SiC in the laser processing. As the laser scanning velocity increased, the temperature on the SiC/SiC surface gradually decreased, and the range of heat affected zone (HAZ) tended to shrink. SiO_2 will be generated on the surface of the material due to the thermal effect produced by laser pulse accumulation, which will cause oxidation on the surface of the material. This oxidation phenomenon gradually became obvious as the laser power and the overlapping rate of laser spot increased. In addition, low overlapping rate of laser spot results in the uneven laser energy irradiated on the material surface. The isotherms of the material surface were interrupted. The edges and sidewalls of the processing region were serrated, and the experimental results were consistent with the simulation results.

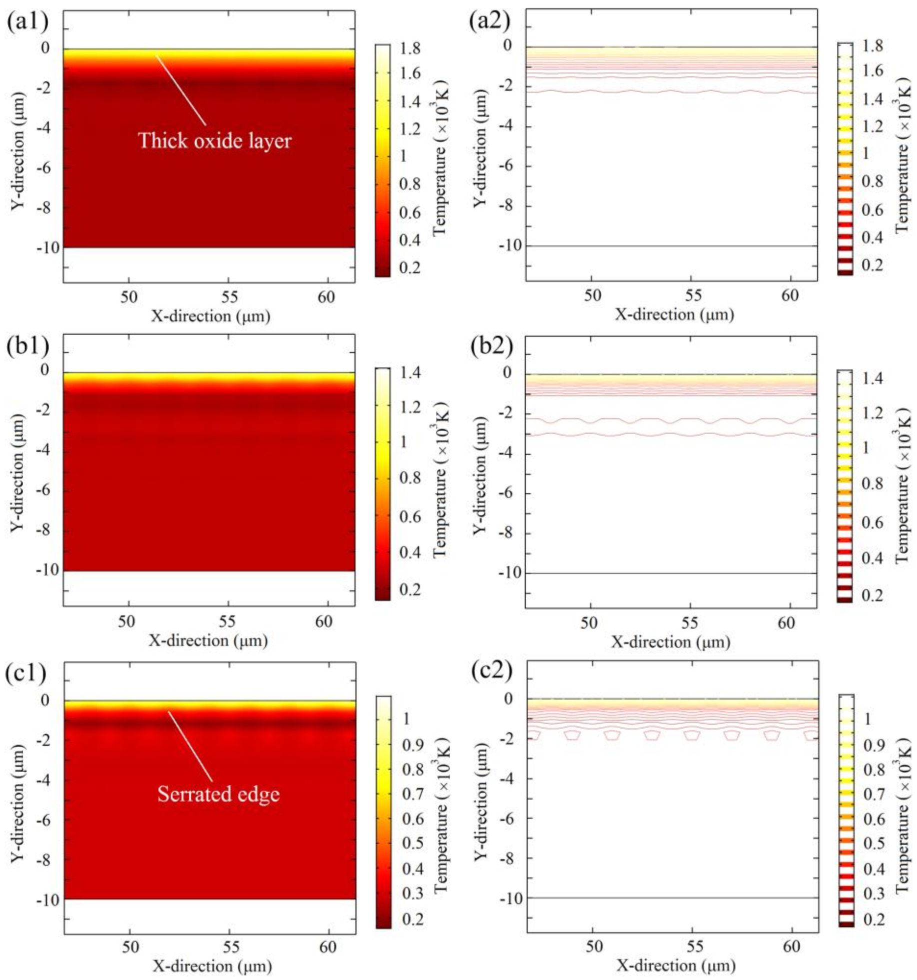

Fig. 15. Surface temperature distribution and isotherm of SiC/SiC in the laser processing: (a) 50 mm/s, (b) 100 mm/s, (c) 200 mm/s.

The SiC material has good oxidation resistance under normal conditions, which is because that a very thin, dense and firmly bonded SiO_2 film is formed on the surface of the SiC material under high temperature, and that the diffusion coefficient of O in the SiO_2 film is very small, so the oxidation of SiC material is very slow. Under such condition, the slow oxidation of the SiC material is called as Passive Oxidation. However, under certain conditions, such as a sufficiently high temperature, a volatile SiO will be formed on the surface of SiC, which will cause rapid oxidation of SiC, and that is active oxidation. The change curve of SiC/SiC surface temperature with laser scanning velocity is shown in Fig. 16. When the laser scanning velocity was 200 mm/s, the maximum temperature of the SiC/SiC surface was about 1273 K, and only a small amount of oxide layer was formed on the surface of the material. When the laser scanning velocity was 100 mm/s, the maximum temperature on the SiC/SiC surface did not exceed 1900 K, and the thickness of the oxide layer slightly increased, but it still belonged to slow passive oxidation. As the laser scanning velocity decreased to 50 mm/s, the maximum temperature on the SiC/SiC surface was close to 2600 K, and active oxidation occurs on the surface of the material, and the oxidation rate increased rapidly.

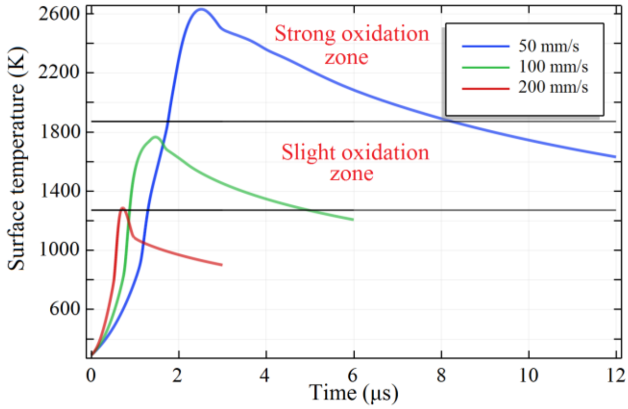

Fig. 16. SiC/SiC surface temperature with different laser scanning velocity.

A microgroove structure was processed on the SiC/SiC surface in a large scale by femtosecond laser with width of 300 μm to verify the rationality of the processing parameters (2 W, 16 J/cm^2, 10 kHz, 100 mm/s). It can be found from the processing experiment of SiC/SiC by femtosecond laser that the contour of the processing region was regular, and that there was neither obvious edge collapse and fiber pull-out normally found in mechanical processing nor the HAZ and oxidation phenomenon normally found in pulsed laser processing, as shown in Fig. 17. The minimum width error of microgroove was up to 2 μm based on the detection by confocal laser microscopy. Comparison between experimental and simulation results indicates that a proper control of processing parameters can help to inhibit oxidative damage of SiC/SiC. In addition, to prevent oxidization, inert gas shielding [26] can be used during the laser processing. Commonly used inert gases include nitrogen and argon, but the former will produce Si_3N_4 with SiC through chemical reaction. Therefore, argon is most suitable for laser processing of SiC/SiC. Due to the cooling and protection effects of argon, the oxidation can be effectively avoided.

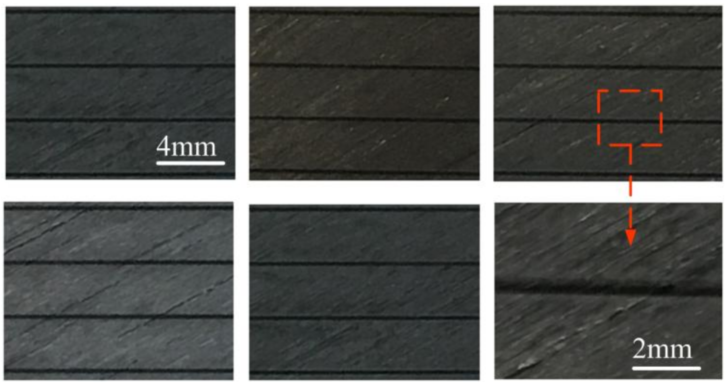

Fig. 17. Verification of the femtosecond laser processing effect.

4 Conclusions

In this study, the high repetition frequency femtosecond laser with a wavelength of 1030 nm was selected to process SiC/SiC. The experimental results were analyzed through theoretical calculation and finite element simulation. Through experiments and simulations, the following conclusions could be drawn. Surface oxidation is a defect which needs to be controlled in the high-frequency femtosecond laser processing of SiC/SiC. The oxidation phenomenon gradually became pronounced with the increase of laser power, repetition frequency and scanning times, but as the scanning velocity increased, the oxidation phenomenon gradually decreased. The overlapping rate of laser spot had a great effect on the processing quality of femtosecond laser. With the increase of the overlapping rate of laser spot, the distance between adjacent pulses decreases, and more heat is accumulated per unit area, which results in an increase in the thickness of the oxide layer. Finally, the rationality of the processing parameters was verified through experiments. A microgroove structure was processed on the SiC/SiC surface in a large scale by femtosecond laser with a width of 300 μm. The experimental results show that the contour of the processing region was regular, and that there was neither obvious edge collapse and fiber pull-out normally found in mechanical processing nor the HAZ and oxidation phenomenon normally found in pulsed laser processing. The minimum width error of microgroove was up to 2 μm.

Acknowledgments

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Investigations on the oxidation phenomenon of SiC/SiC fabricated by high repetition frequency femtosecond laser

Zhaoyang Zhai [a,] *, Chen Wei [a], Yanchao Zhang [a], Yahui Cui [a], Quanren Zeng [b]

[a] *School of Mechanical and Precision Instrument Engineering, Xi'an University of Technology, Xi'an, China;*

[b] *Department of Design, Manufacture and Engineering Management, University of Strathclyde, Glasgow, UK.*

Abstract: SiC/SiC was processed by high repetition frequency femtosecond laser with a wavelength of 1030 nm. The experimental results were analyzed based on the finite element simulation. In the femtosecond laser ablation experiment of SiC/SiC, the processing morphologies under different laser power, repetition frequency, scanning times and scanning velocity were compared. It was found that surface oxidation is an obvious defect in the high-frequency femtosecond laser processing of SiC/SiC, which needs to be controlled. The oxidation phenomenon became more and more obvious with the increased of laser power, repetition frequency and scanning times, while it decreased with the increased of scanning velocity. The parameters of material and laser processing were input into the heat transfer module of the finite element simulation software. The simulation results could intuitively show the formation of different morphological features from the perspective of the temperature field. Finally, the surface oxidation of SiC/SiC was effectively controlled through rationally optimizing the laser processing parameters, and good morphology was obtained. The comparison between simulation and experimental results can help to understand the ablation mechanism of SiC/SiC by high-frequency femtosecond laser, and provide reference for the efficient and precise manufacture of CMC-SiC materials by pulsed laser.

Keywords: High repetition frequency femtosecond laser; SiC/SiC; Surface oxidation; Heat transfer simulation

1 Introduction

As aerospace science and technology changes rapidly, aerospace manufacturing industry is increasingly demanding the performance of materials [1]. Researchers in various countries are placing more and more attention on the new high-performance materials and advanced composite materials for the versatility, structural integrity and design flexibility [2]. Silicon Carbide Ceramic Matrix Composites (CMC-SiC) are featured by low density, high strength, high temperature resistance and corrosion resistance [3], and the reinforcement and toughening effect of the fiber inside the material effectively overcomes the shortcomings of poor fracture toughness of the ceramic material, making this new composite material be widely used in the aerospace field and

* Corresponding author.
E-mail address: zyzhai@xaut.edu.cn (Z.Y. Zhai)

become the development trend of material selection of hot components. CMC-SiC is mainly divided into two types based on the internal fiber composition, namely Carbon Fiber Reinforced Silicon Carbide (C/SiC) and Silicon Carbide Fiber Reinforced Silicon Carbide (SiC/SiC) [4, 5]. The density of CMC-SiC material is only 30% of that of high-temperature alloy, and the operating temperature is higher than that of superalloy by more than 200 K without air cooling and thermal barrier coating. The CMC-SiC components used in aero engines can reduce the weight and the amount of cooling air, improve the inlet temperature and efficiency of the turbine, and reduce the fuel loss and consumption. However, the processed functionalized structure of the material needs to meet the required accuracy to assemble CMC-SiC components into aerospace vehicles [6].

CMC-SiC is difficult-to-machining material with ultra-high hardness. Especially, in the traditional mechanical cutting, the anisotropic CMC-SiC materials are easy to produce burrs, delamination, tearing and chipping in the processing region due to the cutting force [7]. These processing defects directly affect the processing quality and even lead to the scrapping of the parts. The special processing technology differs from traditional processing methods and belongs to non-contact processing. The special processing technology successfully applied to CMC-SiC materials includes water jet machining, ultrasonic processing, electric discharge machining and laser processing [8]. Water jet machining tends to produce fiber pullout on the surface of the material during processing. The accuracy of ultrasonic machining is limited by the amplitude. The recasting layer of electrical discharge machining is obvious. These processes are not qualified for the processing of CMC-SiC materials. Among these processing processes, laser processing has obvious advantages, including high processing quality, non-contact processing, low heat input to materials, and wide application range, and is easy to integrate with numerical control technology to achieve automation [9]. From the perspective of the development of aero engine manufacturing technology, pulsed laser processing will become the mainstream technology for the preparation of surface microstructure of CMC-SiC components in the future [10].

In order to complete high-efficiency processing of large removal in a short time, high-power and long-pulse lasers were used in laser ablation research of CMC-SiC [11]. Liu et al. [12] carried out experimental researches on the thermo-mechanical response of continuous laser irradiated carbon fiber reinforced composites. They found that due to the influence of thermal stress concentration in the laser processing, there was obvious interface delimitation. Because CMC-SiC is woven with multi-layer fibers, it will produce defects in pulsed laser processing, which are different from that of homogeneous materials. Wu et al. [13] conducted ablation experiments on C/SiC with pulsed laser in the direction perpendicular to, parallel to, and axes of fibers, respectively. The results showed that, under the premise of the same processing parameters, the size of the obtained microstructure morphology varied with the scanning direction, and there were processing defects, such as fiber breakage, matrix loss, and microcrack, in the microstructure generated by laser ablation. In the laser ablation process of CMC-SiC materials, because SiC is the main component of CMC-SiC, and it will generate SiO_2 due to the thermal effect caused by the accumulation of laser pulses, which will cause surface oxidation of the material. Wang et al. [14] processed the C/SiC materials with pulsed laser in the air environment. They found that the bottom, side walls and edges of the processing region were covered with white particles. In recent years, scholars focused the precision machining of CMC-SiC by ultrashort pulse laser to suppress the processing defects caused by thermal action on CMC-SiC materials. Wang et al. [15] conducted research on the micro-machining process and mechanism of C/SiC by picosecond laser. Moreno et al. [16] conducted experimental studies on the carbon reinforced materials, which were processed by femtosecond laser. It was found that, under the control of laser parameters, fiber reinforced composites could obtain better processing quality by ultrashort pulse laser due to its short pulse duration and high peak power density.

Since CMC-SiC materials are widely used in the aerospace field and become the development trend of material selection of hot components, now the researches on laser processing of CMC-SiC are still in the initial stage. Most of researches focus on the influence of various laser parameters on the processing effect of CMC-SiC. The causes and improvement methods of processing defects are still unclear, and it is impossible to realize the laser processing of high-quality functional microstructure of CMC-SiC. Surface oxidation [17, 18] is an obvious defect in the laser processing of CMC-SiC, which needs to be controlled. Because the researchers have found that water vapor in the atmosphere reacted with SiO_2 which can generate $Si(OH)_4$ on the surface of CMC-SiC material at high temperature. The properties of CMC-SiC materials will degrade with the continuous reaction. Ultimately, it will lead to damage and failure of CMC-SiC components in the critical condition. Therefore, it is necessary to further research the ablation mechanism of the pulsed laser on the surface microstructure of the material, accurately grasp the formation conditions and evolution mechanism of the surface microstructure, and finally realize the efficient and precise manufacturing of the CMC-SiC material by pulsed laser on a large scale.

2 Experimental method

The performance of CMC-SiC is closely related to its preparation process. The current mainstream preparation processes in the industry are Precursor Infiltration Pyrolysis (PIP), Chemical Vapor Infiltration (CVI), and Melt Infiltration (MI). The surface and internal morphology of CMC-SiC prepared by different processes are quite different. The SiC/SiC sheets used in the experiment were prepared by the MI process, the components prepared by which are relatively compact, with small amount of processing deformation, making it easier to achieve near net shaping. SiC/SiC consists mainly of the outermost SiC deposition layer, the inner SiC matrix, the SiC fiber, and the pyrolytic carbon (PyC) interfacial layer, and there are many tiny pores in the SiC fiber woven structure. The morphology of the experiment material is shown in Fig. 1, and its performance characteristic parameters are shown in Table 1.

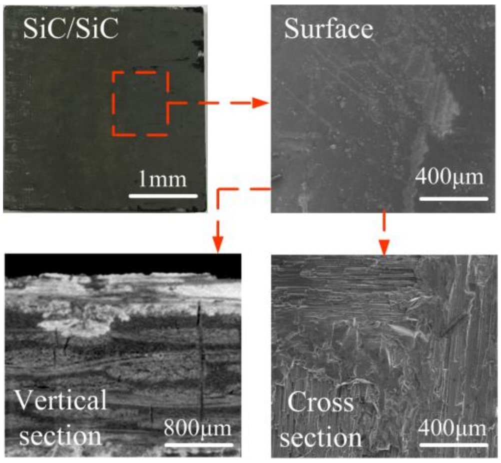

Fig. 1. SiC/SiC surface morphology.

Table 1 Table of material characteristics.

Parameter	Value
Diameter of carbon fiber	12 μm
Thickness of PyC layer	0.2 μm
Density	2.8 g/cm^3
Fiber volume fraction	60 %
Porosity	5 %
Size	30×30×5 mm^3

The Pharos 20 W Yb: KGW all-solid-state femtosecond laser used in the experiment was produced by Light Conversion. The output power, repetition frequency, pulse width and single pulse energy of the femtosecond laser can be directly adjusted through software. The morphology was observed through Hitachi SU8010 field emission scanning electron microscope (FESEM). The specific dimensions were measured by the OLS4000 laser confocal microscope manufactured by Olympus. The Raman scattering spectra of different samples were collected using a Horiba HR800 Raman microscope. The Cambridge Technology EC1000 laser scanning galvanometer system with a JENar 170-1030 F-theta lens was applied in the femtosecond laser processing of SiC/SiC. The experimental light paths are shown in Fig. 2. The processing parameters are presented in Table 2.

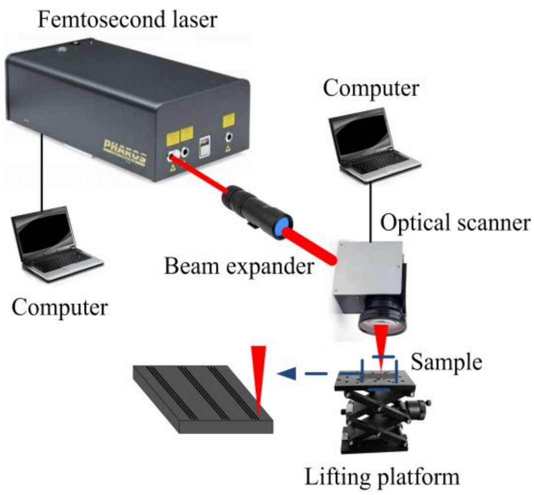

Fig. 2. Light paths in the experiment.

Table 2 Table of processing parameters.

Parameter	Value
Wavelength	1030 nm
Maximum power	20 W
Pulse width	290 fs
Maximum single pulse energy	0.2 mJ
Repetition frequency	1 Hz~200 kHz
Laser mode	TEM_{00} (M^2<1.3)

3 Results and discussion

3.1 Experimental results

A series of femtosecond laser processing experiments was carried out under different parameters to study the processing effect of SiC/SiC surface in detail. Laser wavelength [19, 20] determines the characteristic size of microgroove by affecting the spot size, Rayleigh length and the absorption rate of laser energy. The pulse width of laser has an important influence on the scale and morphology characteristics of laser ablation. In order to focus on the oxidation phenomenon of SiC/SiC fabricated by high repetition frequency femtosecond laser, the main parameters changed in this study include laser power, repetition frequency, scanning times and scanning velocity. The processing effect is shown in Fig. 3. It can be seen from the figure that there was a white oxide accumulation at the edge of the SiC/SiC surface processed by femtosecond laser. Since SiC is the main component constituting CMC-SiC, it will generate SiO_2 due to the thermal effect caused by the accumulation of laser pulses, which will cause surface oxidation of the material. The oxidation phenomenon gradually became pronounced with the increase of laser power, repetition frequency and scanning times, but as the scanning velocity increased, the oxidation phenomenon gradually decreased. When the working state of the laser and the scanning galvanometer was stable, it was found that the processing quality of the SiC/SiC surface processed by high-frequency femtosecond laser was not ideal.

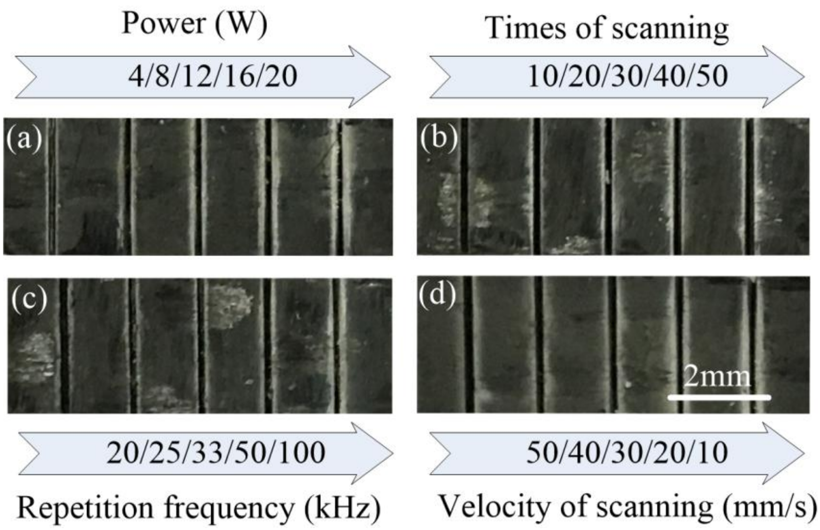

Fig. 3. Surface morphology of SiC/SiC processed by femtosecond laser with different parameters: (a) power, (b) times of scanning, (c) repetition frequency, (d) velocity of scanning.

Surface oxidation is a processing defect which needs to be controlled in the high-frequency femtosecond laser processing of SiC/SiC. The SEM was used to observe the ablation region of femtosecond laser on the SiC/SiC surface, as shown in Fig. 4. After processed by the high-frequency femtosecond laser, there was a large amount of debris at the edge of the processing region, and the debris constantly gathered on the surface with the increase of laser power, repetition frequency, and scanning times. The variation law of the processing morphology with the change of power was taken as an example. When the processing power was 4 W, the debris was dispersed and arranged in granular form; as the power increased, the particles gradually changed into floccule; and when the processing power increased to 20 W, that the dispersed floccule gradually agglomerated, and that the debris accumulated on the surface and gathered continuously under the effect of heat. The reasons for forming the morphology are as follows. First, under the irradiation of low power laser, the material absorbs the laser energy, and the amount of debris formed is small, which is completely dispersed. Second, when the processing power gradually increases, the laser energy increases accordingly, and the amount of debris formed by the absorbing the laser energy significantly increases, the debris is gradually changed from granular form to floccule. Last, as the laser energy further increases, the debris in the dispersed state increases, continuously gathers under the action of thermal effect, and continuously accumulates at the edge of the processing region. The change rule of processing morphology with repetition frequency, scanning times and scanning velocity was similar with it.

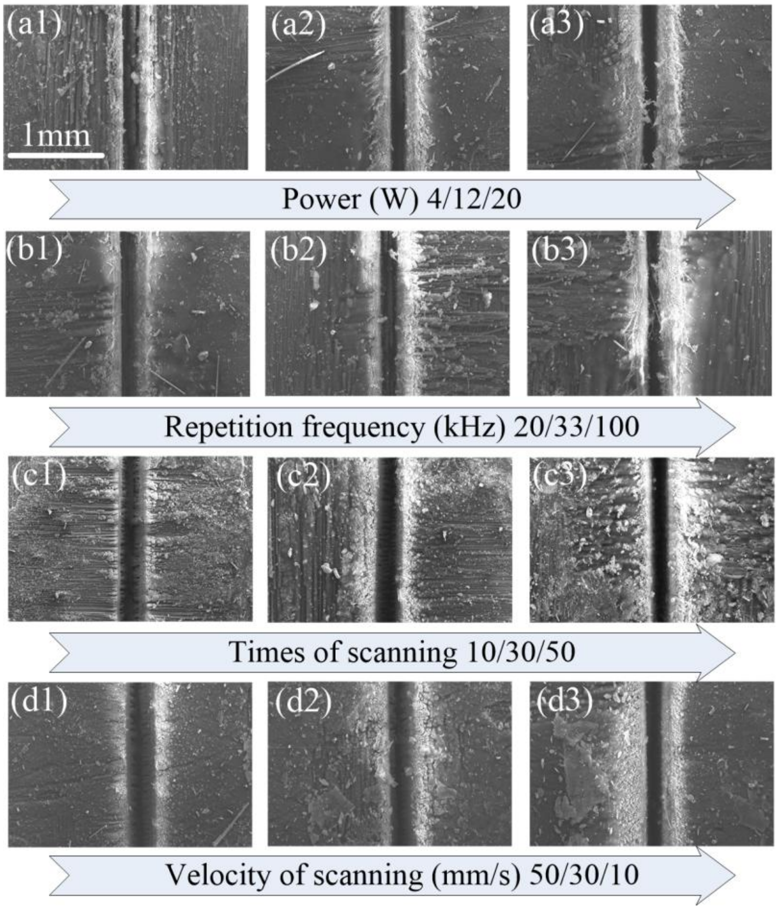

Fig. 4. Surface morphology of SiC/SiC processed by femtosecond laser with different parameters: (a) power, (b) times of scanning, (c) repetition frequency, (d) velocity of scanning.

SiC/SiC was cleaned in an ultrasonic cleaner with alcohol to clearly observe the ablation region, the surface morphology of the cleaned SiC/SiC and the energy dispersion spectrum (EDS) analysis are shown in Fig. 5. It can be seen that the debris adhering to the SiC/SiC surface was removed by ultrasonic cleaning, and that the oxide at the edge of the processing region was still deposited on the SiC/SiC surface after ultrasonic cleaning due to its compact structure. At the edge of the processing region, the material reacted chemically with oxygen in the air after absorbing laser pulse energy, as shown in Eqs. (1), (2) and (3) [21, 22]. Since the laser processing was carried out in the air, it will generate air plasma, which contains O that is easy to combine with positive ions. The content of O combined with positive ions is low in the low-power femtosecond laser processing, and Si and C do not fully combine with oxygen, producing oxides of C and Si. The gaseous products CO and CO_2 will volatilize with the gas stream, but the oxide of Si will adhere to the surface in the form of debris, of which the composition is mainly SiO_2.

$$2O_2(g)+SiC(s)=SiO_2(s)+CO_2(g) \quad (1)$$

$$3O_2(g)+2SiC(s)=2SiO_2(s)+2CO(g) \quad (2)$$

$$O_2(g)+SiC(s)=SiO(g)+CO(g) \quad (3)$$

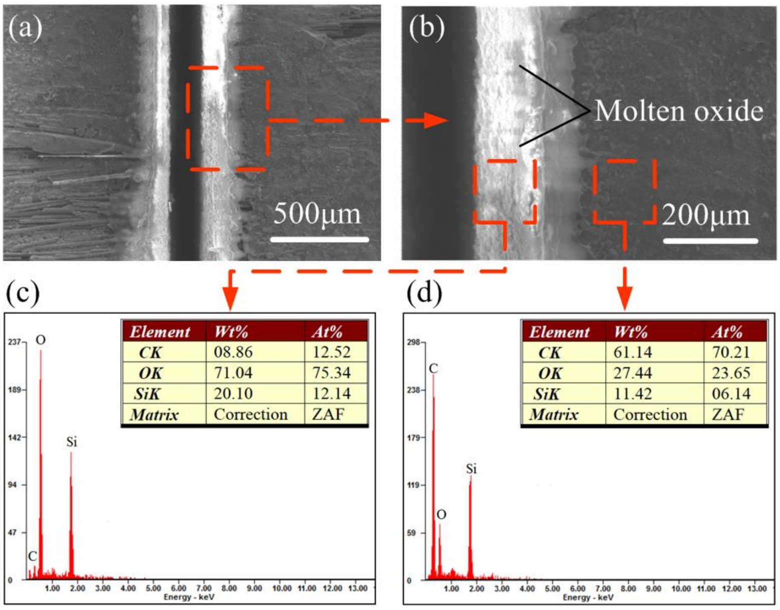

Fig. 5. Surface morphology of SiC/SiC processed by femtosecond laser: (a) low-magnification, (b) high-magnification, (c) EDS analysis of oxide layer, (d) EDS analysis of unmachined surface.

Fig. 6 is the analysis of Raman spectrum before and after processing of SiC/SiC surface. The SiC crystal structure on SiC/SiC surface was 3C-SiC. The area of Raman spectrum showed that, after the femtosecond laser processing, SiC content was reduced, while the relative content of SiO_2 was increased. The existence of D band and G band of SiC/SiC surface were observed in the Raman spectrum, which suggested that, the C of SiC/SiC surface had structure similar with amorphous carbon. This kind of structure displayed certain disorderliness. After femtosecond laser processing, the degree of graphitization was increased.

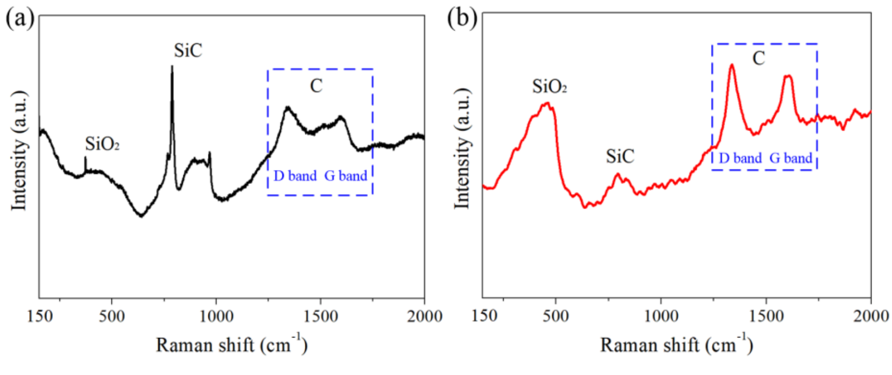

Fig. 6. Raman spectra of the SiC/SiC surface: (a) unmachined surface, (b) oxide layer.

The oxide layer width of the ablation region on the SiC/SiC surface varied with processing parameters, and the curve of variation is shown in Fig. 7. It can be seen that, for surface processing, the laser power is critical to the change in surface morphology and composition after processing. High-power femtosecond laser processing will produce a lot of debris, which will result in a greater damage to the surface morphology and more serious oxidation. Therefore, low-power femtosecond laser is suitable for the surface processing. It can achieve small damage and improve the processing quality while completing the surface processing requirements. The repetition frequency and scanning velocity directly determine the overlapping rate of the laser spot, as shown in Eq. (4). Based on the experimental results, it was found that the overlapping rate of laser spot has a great effect on the processing quality of femtosecond laser. During processing, the removal of materials is mainly due to the accumulation of a large number of pulses. When the overlapping rate of laser spot decreases, the number of effective pulses affecting the material decreases, and therefore, it will directly affect the ablation depth. However, with the increase of the overlapping rate of laser spot, the distance between adjacent pulses decreases, and more heat is accumulated per unit area, which results in an increase in the thickness of the oxide layer. The distribution of laser energy is not directly related to the number of pulses, therefore, the change of the overlapping rate of laser spot does not impact the processing width. In large-scale processing of materials, a large amount of material removal is usually obtained through increasing the laser scanning times.

$$\delta = \left(1 - \frac{v}{D_0 f}\right) \times 100\% \tag{4}$$

In this expression, D_0 is the laser spot diameter at the focal plane, v is the scanning velocity, f is the repetition frequency.

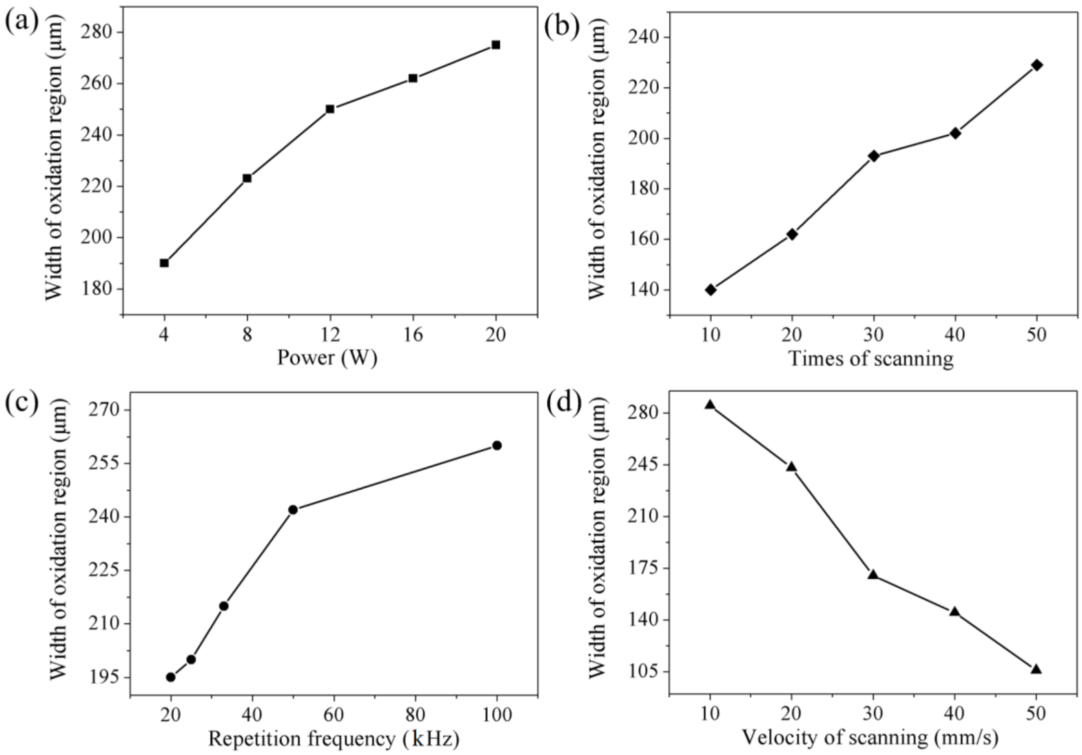

Fig. 7. Oxide layer width of the ablation region on the SiC/SiC surface with different parameters: (a) power, (b) times of scanning, (c) repetition frequency, (d) velocity of scanning.

High-power femtosecond laser processing will produce a lot of debris, which will result in a greater damage to the surface morphology and more serious oxidation. Therefore, low-power femtosecond laser is suitable for the surface processing. It can achieve small damage and improve the processing quality while completing the surface processing requirements. Compared with the high-power femtosecond laser, the low-power femtosecond laser with a processing power of 2 W (16 J/cm^2, 10 kHz, 50 mm/s) ablated on the SiC/SiC surface with less residual debris, making it more suitable for the SiC/SiC surface processing. The processing morphology is shown in Fig. 8. There was still a small amount of oxide accumulated at the edge of the SiC/SiC surface processing region.

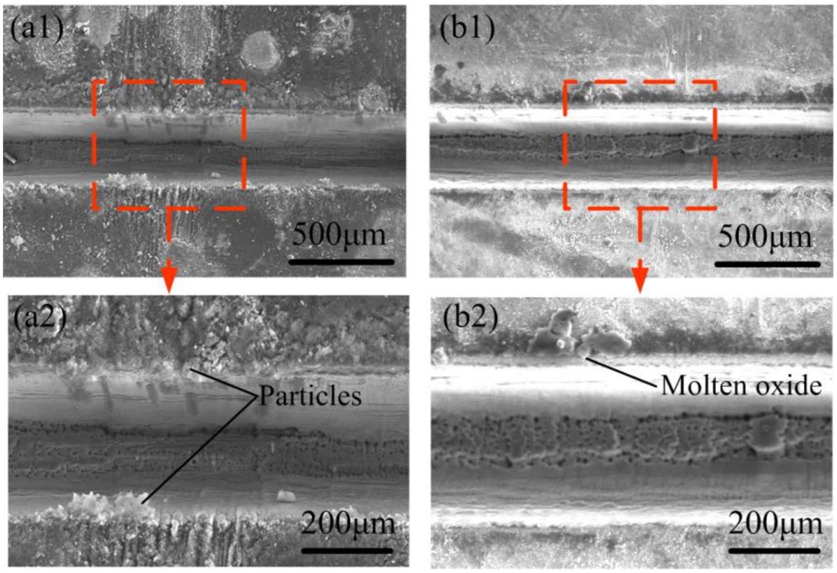

Fig. 8. Surface morphology of SiC/SiC processed by femtosecond laser: (a) uncleaned, (b) cleaned.

In order to further control the surface oxidation of SiC/SiC and obtain better morphology quality, the overlapping rate of laser spot was controlled and the distance between adjacent pulses was reduced by adjusting the repetition frequency and scanning velocity of the laser, thereby reducing the heat accumulation in the unit area during laser processing. Fig. 9 shows the SiC/SiC morphology processed under different scanning interval. It was found that the surface oxidation of SiC/SiC was effectively controlled, and that no oxide accumulation occured at the edge of the processing region, good morphology quality was obtained. Calculated results showed that the overlapping rate of laser spot was 75% (2 W, 16 J/cm^2, 10 kHz, 100 mm/s).

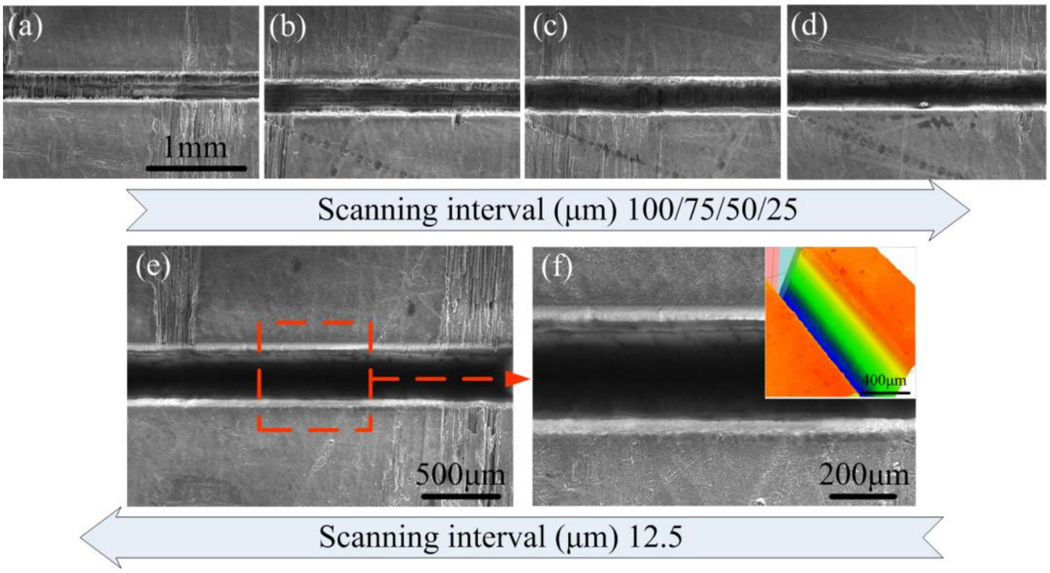

Fig. 9. Surface morphology of SiC/SiC processed by femtosecond laser with different scanning interval: (a) 100 μm, (b) 75 μm, (c) 50 μm, (d) 25 μm, (e) 12.5 μm, (f) high-magnification.

It should be noted that, in the laser processing of SiC/SiC, better quality could not be obtained with lower overlapping rate of laser spot. Lower overlapping rate of laser spot will result in a decrease of the number of effective pulses acting on the material. It directly affects the ablation depth and the morphology in the ablation region. The processing morphology is shown in Fig. 10. Lower overlapping rate of laser spot will result in uneven laser energy received at the surface of the material, and even separation between the spots, leading to different material removal amount. Therefore, the edges and sidewalls of the processing region are serrated, and this morphology is more pronounced as the overlapping rate of laser spot decreases.

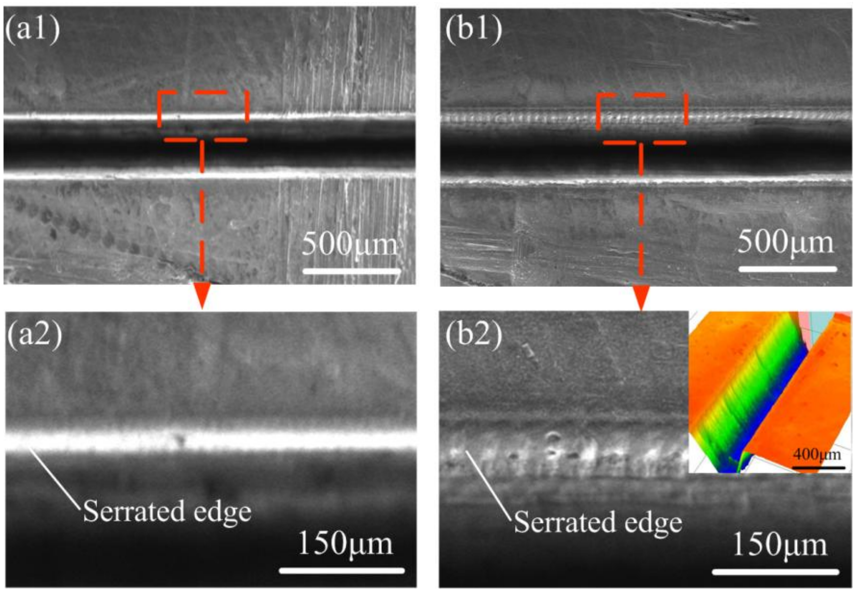

Fig. 10. Surface morphology of SiC/SiC processed by femtosecond laser with different scanning velocity: (a) 150 mm/s, (b) 200 mm/s.

In addition, because linear polarized beam was used in the experiment, waviness features can be observed in a magnified SEM micrograph in the part of the bottom and wall of processing region, as shown in Fig. 11. These waviness features are generally described as ripples or laser induced periodic surface structures [23, 24] for other materials. A feasible way to avoid the formation of surface ripples is to convert the linear polarization state of laser into circular polarization state through the use of a 1/4 wave plate in the light paths.

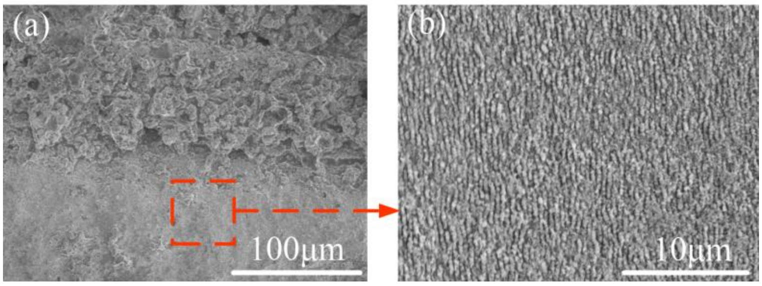

Fig. 11. Laser induced periodic surface structures: (a) low-magnification, (b) high-magnification.

The material removal induced by a femtosecond laser is a complicated physicochemical process, accompanied by the absorption of laser energy, thermal conduction, avalanche ionization, plasma expansion, liquid phase blasting, and other processes. SiC [25] has a 3.02 eV band gap and the photon energy of a laser pulse at 1030 nm is 1.2 eV, so ionization will be achieved only through multi-photon non-linear absorption. Ionization of SiC takes place after absorbing the multi-photon energy, and the number of free electrons will increase by great leaps due to the avalanche effect to produce plasma. The femtosecond laser has a short pulse width, so the influence of plasma shielding can be effectively avoided. Because the action time of femtosecond laser is much smaller than the lattice relaxation time, the thermal energy converted from photon energy after absorbed by SiC can only be conducted inside the crystal lattice, and has little thermal effect on the surrounding materials. However, in practical applications, it can be found from the experimental results that femtosecond laser processing also has a thermal effect on the surrounding materials due to the existence of pulse accumulation effect. The ablation principle of the femtosecond laser on the SiC/SiC surface is shown in Fig. 12. From the perspective of laser energy, the ablation rate of SiC/SiC by femtosecond laser is composed of two parts, namely photochemical ablation rate and photothermal ablation rate. When the high-frequency femtosecond laser irradiates the surface of SiC/SiC, photothermal action and photochemical action simultaneously act on the material. When the laser energy and the overlapping ratio of laser spot are small, the interval between pulses is smaller than the thermal relaxation time, and the photochemical action is dominant. As the laser energy and the overlapping ratio of laser spot increase, the photothermal effect gradually dominate. In general, this thermal effect is disadvantageous in femtosecond laser processing, which will lead to the decline in processing accuracy and surface quality.

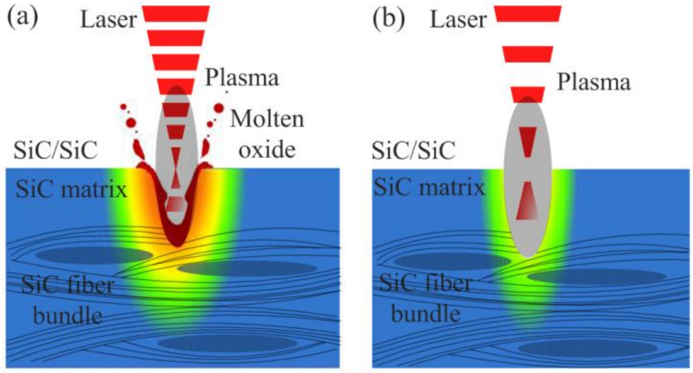

Fig. 12. Schematic diagrams of ablation mechanisms: (a) photothermal effect, (b) photochemical effect.

In the SiC/SiC surface processing of femtosecond laser, when the laser energy and the overlapping ratio of laser spot are large, the photothermal action will make the material melt, and the flying molten matter will disperse and shrink into particulates due to surface tension, thus forming the observed sparking phenomenon. The accumulated heat per unit area can be reduced by adjusting the laser power and the overlapping rate of laser spot. Under action of photochemistry, SiC/SiC ionizes after absorbing multiphoton energy and forms plasma. The ablation process of femtosecond laser on the SiC/SiC surface is shown in Fig. 13.

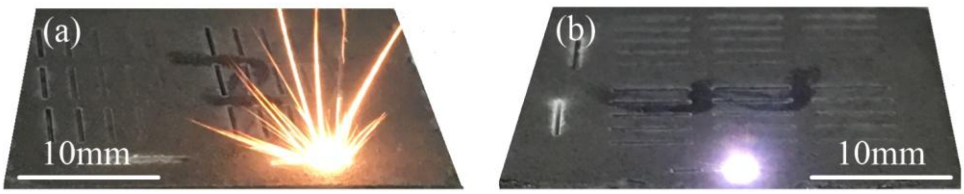

Fig. 13. Ablation process of femtosecond laser on the SiC/SiC surface: (a) photothermal effect, (b) photochemical effect.

3.2 Theoretical analysis and verification

High-frequency and high laser power are conducive to improving the processing efficiency, but at the same time bring new problems. When the overlapping ratio of the laser pulses is too large, the heat accumulation between the pulses becomes more and more significant. In general, this thermal effect is disadvantageous in femtosecond laser processing, which will lead to the reduction in processing accuracy and surface quality. Researchers can use the complex geometric models in the heat transfer modules of COMSOL Multiphysics to study the effects of heating and cooling processes on materials. This module can simulate the heat transfer mechanisms of materials, including conduction, convection, and radiation. The heat transfer simulation can be performed in three-dimensional coordinate systems to solve the steady and transient problems. The specific solution steps in this study are as follows: constructing a two-dimensional geometric model of the SiC layer on the SiC/SiC surface; defining the properties of the SiC material, and selecting solid heat transfer as the analysis type; defining the boundary conditions and initial values based on the laser processing parameters; setting the laser source to move along the scanning direction at a constant velocity; applying the laser heat source load to the SiC layer of the SiC/SiC surface in the type of heat flow density. The simulation model is shown in Fig. 14. The geometric model was meshed, and the transient solver was selected for calculation, and finally the results were visualized. In the simulation model, the part of laser energy used for thermal effect was controlled by a coefficient.

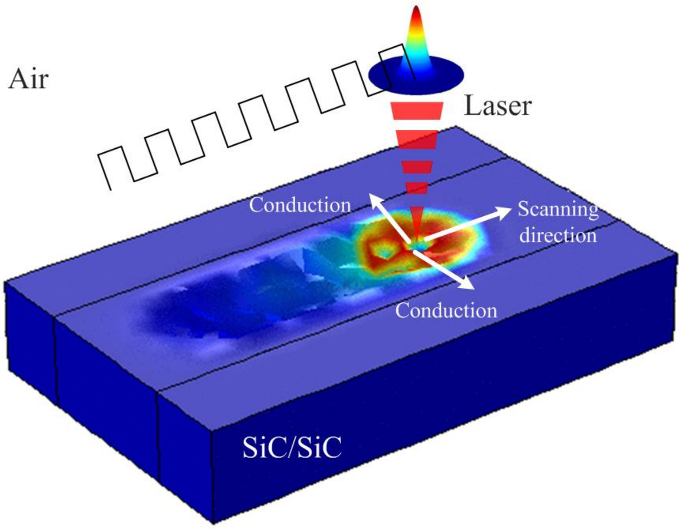

Fig. 14. Model of laser processing simulation of SiC/SiC.

Fig. 15 shows the surface temperature distribution and isotherm of SiC/SiC in the laser processing. As the laser scanning velocity increased, the temperature on the SiC/SiC surface gradually decreased, and the range of heat affected zone (HAZ) tended to shrink. SiO_2 will be generated on the surface of the material due to the thermal effect produced by laser pulse accumulation, which will cause oxidation on the surface of the material. This oxidation phenomenon gradually became obvious as the laser power and the overlapping rate of laser spot increased. In addition, low overlapping rate of laser spot results in the uneven laser energy irradiated on the material surface. The isotherms of the material surface were interrupted. The edges and sidewalls of the processing region were serrated, and the experimental results were consistent with the simulation results.

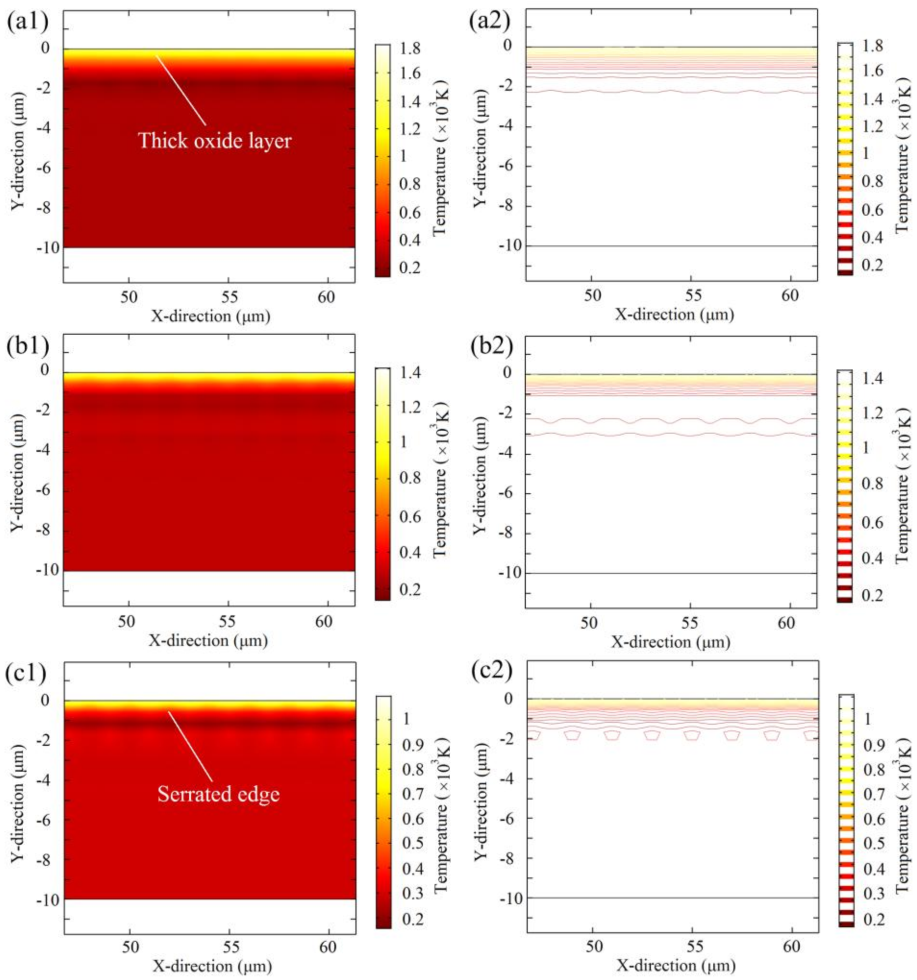

Fig. 15. Surface temperature distribution and isotherm of SiC/SiC in the laser processing: (a) 50 mm/s, (b) 100 mm/s, (c) 200 mm/s.

The SiC material has good oxidation resistance under normal conditions, which is because that a very thin, dense and firmly bonded SiO_2 film is formed on the surface of the SiC material under high temperature, and that the diffusion coefficient of O in the SiO_2 film is very small, so the oxidation of SiC material is very slow. Under such condition, the slow oxidation of the SiC material is called as Passive Oxidation. However, under certain conditions, such as a sufficiently high temperature, a volatile SiO will be formed on the surface of SiC, which will cause rapid oxidation of SiC, and that is active oxidation. The change curve of SiC/SiC surface temperature with laser scanning velocity is shown in Fig. 16. When the laser scanning velocity was 200 mm/s, the maximum temperature of the SiC/SiC surface was about 1273 K, and only a small amount of oxide layer was formed on the surface of the material. When the laser scanning velocity was 100 mm/s, the maximum temperature on the SiC/SiC surface did not exceed 1900 K, and the thickness of the oxide layer slightly increased, but it still belonged to slow passive oxidation. As the laser scanning velocity decreased to 50 mm/s, the maximum temperature on the SiC/SiC surface was close to 2600 K, and active oxidation occurs on the surface of the material, and the oxidation rate increased rapidly.

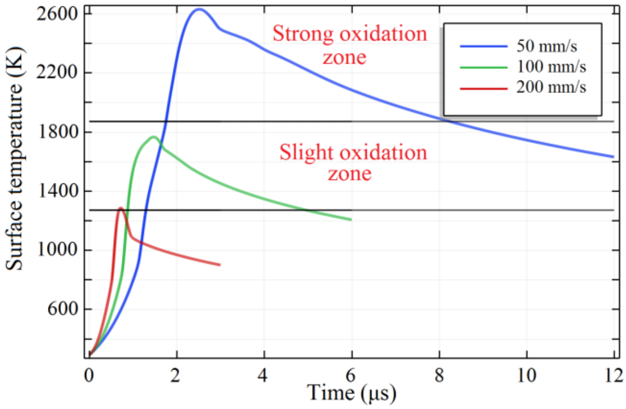

Fig. 16. SiC/SiC surface temperature with different laser scanning velocity.

A microgroove structure was processed on the SiC/SiC surface in a large scale by femtosecond laser with width of 300 μm to verify the rationality of the processing parameters (2 W, 16 J/cm^2, 10 kHz, 100 mm/s). It can be found from the processing experiment of SiC/SiC by femtosecond laser that the contour of the processing region was regular, and that there was neither obvious edge collapse and fiber pull-out normally found in mechanical processing nor the HAZ and oxidation phenomenon normally found in pulsed laser processing, as shown in Fig. 17. The minimum width error of microgroove was up to 2 μm based on the detection by confocal laser microscopy. Comparison between experimental and simulation results indicates that a proper control of processing parameters can help to inhibit oxidative damage of SiC/SiC. In addition, to prevent oxidization, inert gas shielding [26] can be used during the laser processing. Commonly used inert gases include nitrogen and argon, but the former will produce Si_3N_4 with SiC through chemical reaction. Therefore, argon is most suitable for laser processing of SiC/SiC. Due to the cooling and protection effects of argon, the oxidation can be effectively avoided.

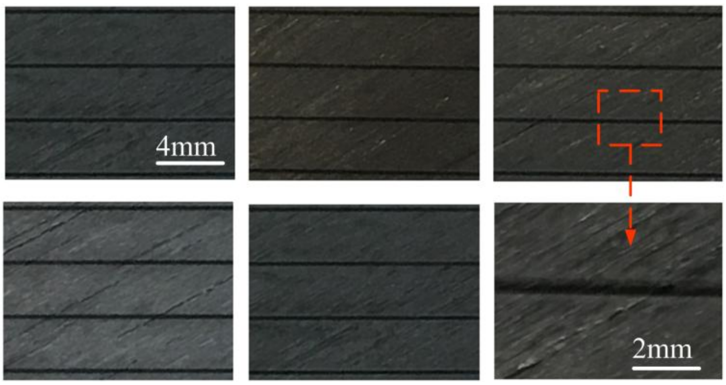

Fig. 17. Verification of the femtosecond laser processing effect.

4 Conclusions

In this study, the high repetition frequency femtosecond laser with a wavelength of 1030 nm was selected to process SiC/SiC. The experimental results were analyzed through theoretical calculation and finite element simulation. Through experiments and simulations, the following conclusions could be drawn. Surface oxidation is a defect which needs to be controlled in the high-frequency femtosecond laser processing of SiC/SiC. The oxidation phenomenon gradually became pronounced with the increase of laser power, repetition frequency and scanning times, but as the scanning velocity increased, the oxidation phenomenon gradually decreased. The overlapping rate of laser spot had a great effect on the processing quality of femtosecond laser. With the increase of the overlapping rate of laser spot, the distance between adjacent pulses decreases, and more heat is accumulated per unit area, which results in an increase in the thickness of the oxide layer. Finally, the rationality of the processing parameters was verified through experiments. A microgroove structure was processed on the SiC/SiC surface in a large scale by femtosecond laser with a width of 300 μm. The experimental results show that the contour of the processing region was regular, and that there was neither obvious edge collapse and fiber pull-out normally found in mechanical processing nor the HAZ and oxidation phenomenon normally found in pulsed laser processing. The minimum width error of microgroove was up to 2 μm.

Acknowledgments

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Graphical Abstract (for review)