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Study on Physical and Chemical Properties of Industrial Silicon Slag

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Abstract

Silicon slag is a secondary refining byproduct from industrial silicon. The content of industrial silicon in silicon slag is about 20% , which has extremely high economic value. To better achieve the recovery and reuse of industrial silicon slag, the morphology of industrial silicon slag, the occurrence state of elements and especially the interfacial structure between silicon and slag were deeply studied in this paper. The macro and micro morphology and surface composition distribution of the silicon slag were observed by microscope, SEM-EDS and Raman spectroscopy. The phase and composition of the silicon slag were analyzed by XRF and XRD. The results showed that the purity of silicon particles in silicon slag is high up to 99% . The size and shape of silicon in silicon slag were quite different. The interface between silicon and slag is clear and there is no obvious two-phase transition zone, which is conducive to the recycling of silicon. The crushing behavior of silicon slag under different pressure was investigated. These results provide a theoretical basis for further crushing silicon slag and recovering silicon particles. When silicon slag was crushed under certain pressure, the fracture surface of large-size silicon was mostly silicon-silicon interface. Therefore, in order to realize the complete dissociation of slag and silicon, the size of the crushing particle needs to be small enough. In this paper, the physical and chemical properties of industrial silicon slag were studied, which provides a theoretical basis for the efficient separation and recovery of silicon in the slag.

1. Introduction

Solar energy has gained increasing attention due to its sustainability in the word. More than 80% of commercial solar cells are made of silicon wafers[1]. At present, the main methods of industrial silicon purification are directional solidification[2–5], oxidation refining[6, 7], electron beam method[8],chemical leaching and[9, 10] so on. The oxidative refining is the main method for the secondary refining of industrial silicon. Its essence is to oxidize the impurity elements in the melt by slag forming constituent. Industrial silicon is generally more than 99% pure and contains impurities such as P, B, Al, Fe and Ca[11, 12]. In order to achieve the purity of solar level silicon, the impurities are generally removed by the oxidation refining method, whose essence is to make the impurities in the melt oxidized by slag-making agent enter into the slag phase. In the secondary refining of industrial silicon, slag system is the key to determine the removal efficiency[13–15]. Common slag systems include Na_2O-SiO_2[16], Si-Al-Ca[17], CaO-SiO_2[13], SiO_2-Al_2O_3[18] etc. Wang et al. studied the oxidation behavior and the phase evolution of metallurgical silicon slag by means of phase variation under the non-isothermal and isothermal conditions[19]. The rates of mass transfer between liquid silicon and CaO-SiO_2 slag with impeller stirring at 1823 K was studied. The occurrence of transient interfacial phenomena related to the mass transfer of calcium has been observed [20]. Qian et al studied the mechanism of Si crystal growth and solid-liquid interface migration and its correlation with impurities removal in directional solidification refining with Al-Si alloy [21]. Some studies also show that industrial silicon slag contains a certain proportion of silicate and glass phase, which is a better raw material for porous microcrystalline glass[22]. However, the remaining elemental silicon in the slag is still wasted. Jing et al. described one method to extract metallic silicon from waste silicon slag with the process of hand sorting, separation by machine, burdening and smelting[23]. The study shows that the silicon in slags can be recovered by flotation with HF and a frother[24]. Zhou et al. studied the physicochemical purification mechanism of silicon in silicon slag, and proposed the addition of Cl-containing calcium silicate slag-forming agent to the raw material in combination with electromagnetic separation method to achieve effective purification of metal silicon[14]. The method to extract elemental silicon from industrial slag by refining furnace slag was tested in some factories and low economic efficiency is its biggest problem. Slag refining not only consumes a lot of energy, but also has a low recovery rate of silicon resources.

A lot of silicon was carried in the process of discharging slag. There is approximately 15–20% industrial silicon in the discharged silica residue and then about 600,000 tons of industrial silicon were packed into the slag produced each year[23]. At present in China, a large amount of silicon slag was used for road paving or as a waste accumulation, which makes the metal silicon resources in the slag phase seriously wasted[25, 26]. Therefore, the recycling of silicon in silicon slag has been received extensive attention. Silicon recycling not only saves energy and protects the environment, but also has economic benefits.

The development of a simple and feasible process to realize silicon recycling is a major challenge in the silicon industry. In order to overcome this difficulty and put forward the solution ideas, we carried out the analysis of the composition and structure of silicon slag. In order to understand silicon/slag dissociation performance, we focused on the interface structure between silicon and slag. This work will support the further optical sorting and flotation processes investigation.

2. Methods

The industrial silicon slag was obtained from a metal factory in Yunnan Province. The industrial silicon produced by the factory was from oxidation refining.

In order to analyze the interface characteristics and crushing performance of industrial silicon slag more clearly and intuitively, the industrial silicon slag was firstly cut into pieces by cutting machine and the surface is then polished. The micro morphology and energy spectrum analysis were carried out by microscope, REGULUS 8100 scanning electron microscope and Horiba Labram HR800 Raman spectrum.

The samples were crushed into powder and sieved through 200 mesh screen. The phase analysis was carried out on D8 focus X-ray diffractometer (XRD). The composition of silicon slag and metal silicon was determined using S8 TIGER X-ray fluorescence spectrometer (XRF). The pressure crushing experiment is carried out by a press machine(FW-4A). The same amount of silicon slag was selected to be broken under different pressures. The degree of breaking is observed and the micro morphology after breaking is analyzed.

3. Results And Discussion

3.1 Chemical composition and phase analysis of silicon slag

XRF and XRD were used to test the silica slag and the separated silica particles. The results were given in Table 1 and Fig. 1, respectively.

In Table 1, it can be seen that the content of silicon element in industrial silicon slag is over 48%, and the content of Ca and Al are also relatively high. We can learn from the XRD test (Fig. 1) that some silicon in industrial silicon slag exists in the form of SiC, $Ca_2A1_2SiO_7$. The purity of the metallic silicon particles separated from silicon slag is higher than 99%, which meets the basic criteria of industrial silicon and still has extremely high recycling value.

Table 1
The XRF result for silicon particles and silicon slag

Element	Silicon slag (wt %)	Silicon (wt %)
Si	48.57	99.01
Ca	30.68	0.36
Al	19.68	0.42
Fe	0.31	0.15
Ti	0.16	0.00
S	0.15	0.03
P	0.14	0.00
Mg	0.13	0.00
Ba	0.08	0.00
Sr	0.07	0.00
K	0.05	0.00
Cr	0.02	0.02

Industrial silicon purification is mainly based on oxidation refining. In this process, slagging agents oxidize impurity elements in the melt to enter the slag phase, and the metal and slag reach thermodynamic equilibrium, thus achieving the impurity removal. At present, the commonly used oxidants are mainly O_2. Solid oxidant SiO_2 and synthetic slag CaO-Al_2O_3-SiO_2, etc., and sometimes CaF_2 or Na_2O etc. are also introduced to reduce the viscosity of the refining system. This is consistent with the results of XRF and XRD. The content of Ca in the silicon slag is high and it will diffuse into the metallic silicon in the silicon slag at high temperature, resulting in an increase of Ca content in the metallic silicon.

Meanwhile, impurity elements such as Ca, Al and the like in the silicon are oxidized and floated on the surface of the silicon fliud by gas to form scum during oxidation refining. It is found that, besides the oxides Si, Ca and Al, there also exists SiC in the silicon slag. It is generated by the reaction of SiO and C when the furnace temperature reaches 1500–1800℃ during oxidation refining[27]. Since the industrial silicon slag has not only high content of industrial silicon, but also high purity, meeting the basic standard of industrial silicon, so it still has extremely high recycling value.

3.2 Morphology Analysis of Silicon Slag and Metal Silicon Inclusion in Silicon Slag

Figure 2(a) shows that the particle size of the metal silicon mixed in the industrial solid waste silicon slag It can be seen from Fig. 2(b) that some industrial silicon in the silicon slag can be completely dissociated varies from several millimeters to microns, or even smaller, after preliminary crushing, but most industrial silicon with smaller particle size is still closely connected with the silicon slag. Although the slag phase and the silicon phase are both liquid at high temperature in the refining process, they have obvious and clear interface after being cooled into solid (Fig. 2c). This maybe due to the different properties of the slag and silicon. In the molten state, silicon is a metallic liquid, while slag resembles molten salt. According to the similar compatibility principle, they are not easy to penetrate each other.

Figure 3 shows the micromorphology of industrial silicon slag after cutting and polishing treatment. There is an obvious difference between the slag and silicon. It can be seen that there are obvious scratches on the surface of silicon phase after polishing, but there is no obvious change in slag phase (Fig. 3). Through this phenomenon, we can draw a conclusion that the brittleness of silicon is greater than that of silicon slag and silicon is less hard.

3.3 Interface analysis of silicon slag

In order to study the distribution of elements and the interfacial structure in industrial silicon slag, the analysis of silicon slag samples by SEM, EDS energy spectrum and Raman spectrum was carried out. From Fig. 4, clear silicon and slag interfaces can be observed at different magnification, even at 10 microns. The main impurity elements, such as Ca, Al, O, are basically distributed in the slag phase. The transition layer of silicon and slag is almost non-existent from the almost vertical lines in the distribution of elements (Fig. 4d). Figure 4 also shows that the surface of silicon phase is smooth while the slag phase is relatively rough. EDS energy spectrum further confirms the distribution of impurity elements in silicon slag (Fig. 5). The distribution of other elements is almost invisible on the silicon side, which further indicates that the inclusion of granular silicon in the slag is of high purity. Compared the EDS line scanning energy spectrum of the silicon slag with the EDS mapping test results of the silicon slag in Fig. 5, there is a significant difference between the slag and silicon at the interface of the silicon slag, and the changing trend of the element content at the interface is very obvious. There is no transition phase and the boundary is clear. Meanwhile, the existence of interface difference is further proved by Raman spectrum test (Fig. 6). The silicon phase has only one single peak, which is attributed to the Raman spectral peak of the silicon. The slag phase shows complex multiple peaks, which indicates that the slag phase is composed of a variety of compounds. In the fine structure scanning area (Fig. 6b), the clear interface between slag and silicon in the block is again demonstrated.

Different test methods have proved that in silica slag, silica and slag have a clear interface, and no obvious transition structure exists in the interface area, which is very conducive to further cleavage and separation of silica and slag.

3.4 Silicon slag crushing test

In order to observe the cleavage of silica slag under different pressures, experiments were carried out with the same batch of materials. Silica slag of equal quality is selected to be tested with different pressures, and then sieved through 50 mesh sieve. The experimental results are shown in Fig. 7. The data shows that the silicon slag with the particle size smaller than 50 mesh accounts for about 40% under the pressure 4 MPa. As the pressure increases, the particle size tends to decrease and it accounts for about 55% at 8 MPa. In order to achieve efficient separation and recovery of silicon in the process of silicon slag crushing, it is necessary to ensure the dissociation degree of silicon monomer. From Fig. 8 (a)-(c), most cleavage surfaces are produced by silicon silicon splitting, which further indicates that the silicon phase is brittle. Although the interface between the two phases is clear, the interaction between the two phases is strong. Further research is needed to use process enhancement techniques to crack this force.

3.5 The refining of separated silicon

The crushed silicon slag obtained in the Fig. 8 was manually sorted to obtain the particles containing a large amount of silicon. However, just as the above study found, the resulting silicon particles still have some residue on them. In order to test whether the industrial purity of block silicon can be obtained, the silicon particles obtained above were smelted and observed. The manually selected silicon was placed in the crucible and calcined at 1550 ^{o}C, keeping the temperature for 30 min and then cooled to room temperature. The state after sintering is shown in Fig. 9.

It can be seen that the further separation of industrial silicon and slag can still be realized after high temperature melting without adding any oxidant. The bulk of the silicon is concentrated in the middle of the crucible, while a small amount of slag accumulates around the silicon and clings to the walls of the crucible. From the cut surface, it can be seen that the slag is also separated from the silicon without the stirring of the gas, which is attributed to the formation of the slag phase itself, rather than the re-formation in the refining process. This is a very important phenomenon. This means that the silicon does not need to be separated to the point where there is no silica residue at all. A small amount of slag can be enriched and removed by simple smelting. As shown in Fig. 10, SEM test is carried out after cutting the remolded silicon. Compared with the SEM of the cut surface of the silicon slag after secondary refining (Fig. 4), there is no obvious difference at the interface and the interface characteristics are similar. The slag phase plays the role of oxidant again, making the industrial silicon further been purified.

4. Conclusions

This paper mainly studies the interface characteristics of industrial silicon slag, analyzes the interface differences between slag and silicon and the crushing characteristics. The purity and content of metal silicon mixed in industrial silicon slag show a very high recycling value. The impurities in the slag are mainly O, Al, Ca, Fe, and so on. The interface between the silicon phase and the slag phase is distinct. No obvious transition zone was observed in the interface structure. The silicon is firmly bound to the slag and no interface dissociation under different pressures was observed. Further research is needed to realize interface dissociation using the reinforcement technique. The silicon obtained by manual sorting can be separated from residual slag by smelting, which is beneficial to the recovery and utilization of metallic silicon in industrial silicon slag.

Declarations

Compliance with Ethical Standards ""For "Ethical statement", This article does not contain any studies with human participants or animals performed by any of the authors. In this experiment, we did not collect any samples of human and animals."

Conflict of Interest

We declare that we have no conflict of interest.

Consent to Participate

Not applicable.

Consent for Publication

Not applicable.

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Availability of Data and Material

All data generated or analysed during this study are included in this published article.

Author Contributions

Dan Qiao: Formal analysis, Validation, Data curation, Writing-original draft, Writing-review & editing. Shuai Liang: Conceptualization, Resources, Visualization, JianGuo Zhao: Conceptualization, Resources, Visualization, XiuJing Peng: Conceptualization, Resources, Visualization. Yong Nie: Writing-review & editing, YeXin Li: Writing-review & editing. Yu Cui：Conceptualization, Resources, Writing-review & editing, Visualization, Validation, Supervision. GuoXin Sun：Conceptualization, Resources, Writing-review & editing, Visualization, Validation, Supervision.

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Figures

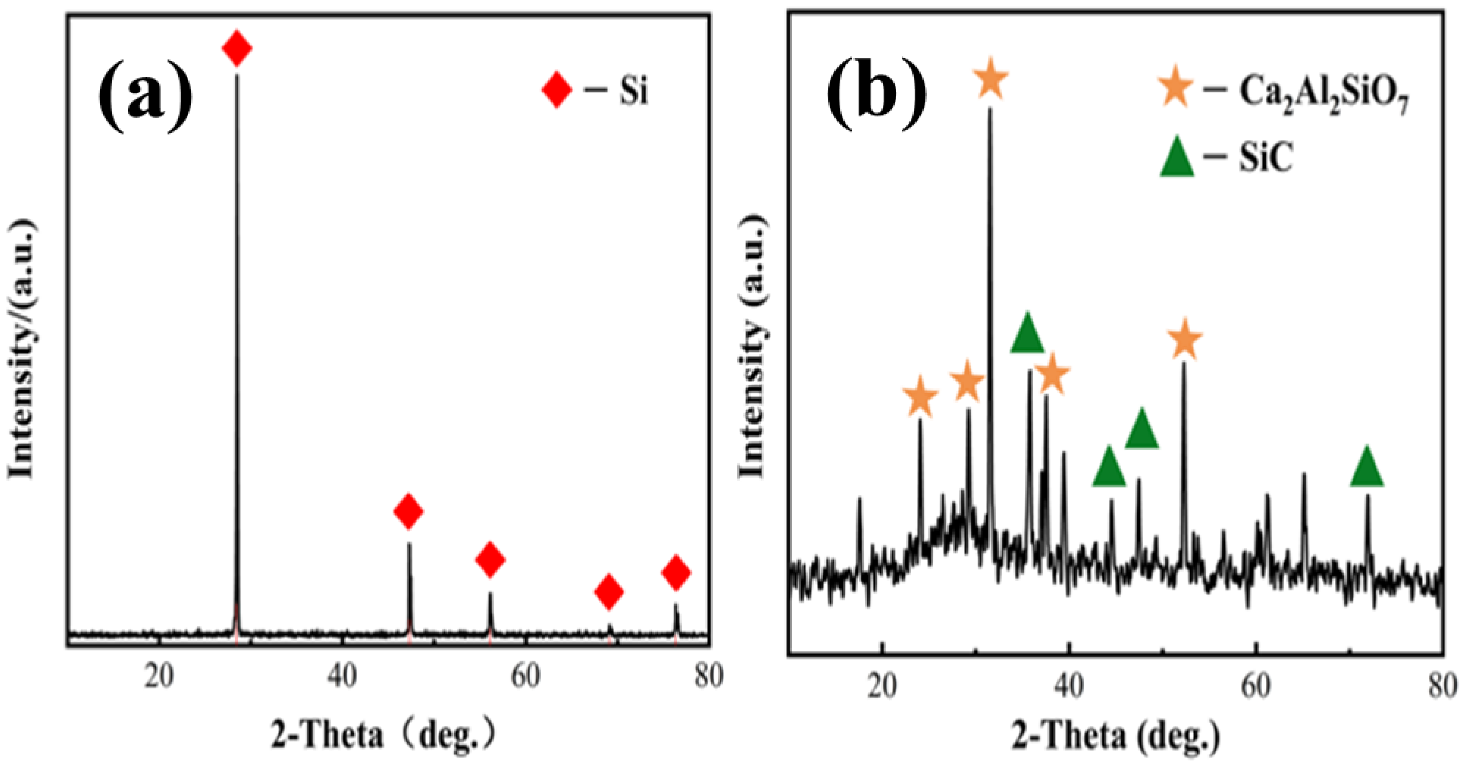

Figure 1

XRD of silicon particles and silicon slag

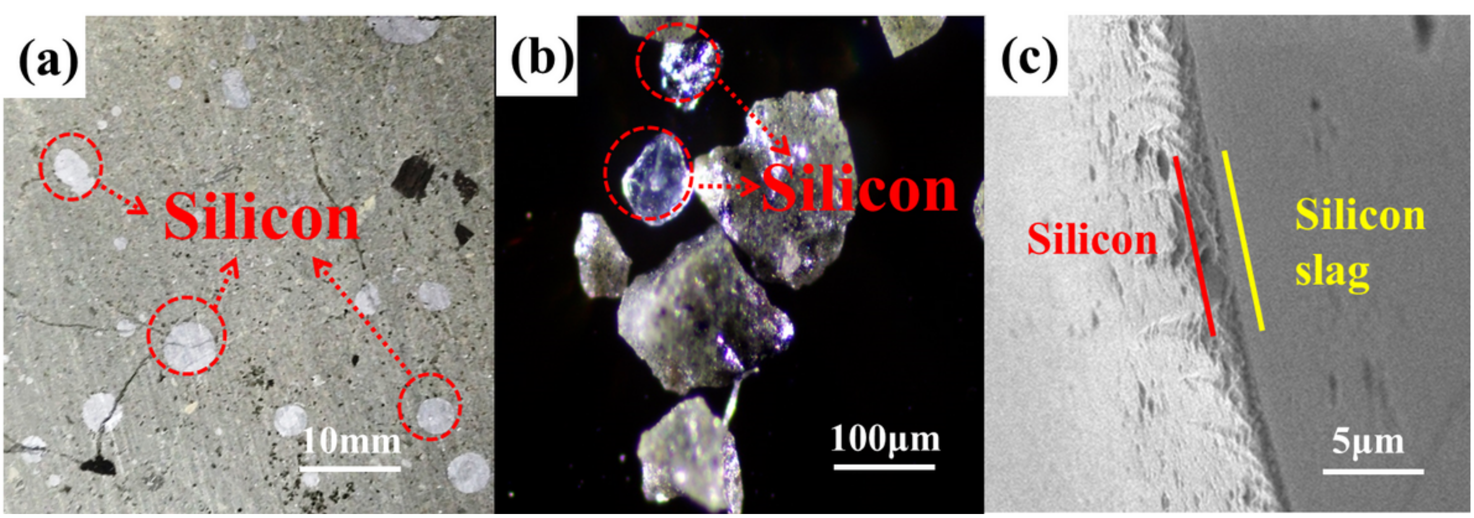

Figure 2

Use different testing methods for silicon slag. (a) Camera(b) Microscope(c) SEM

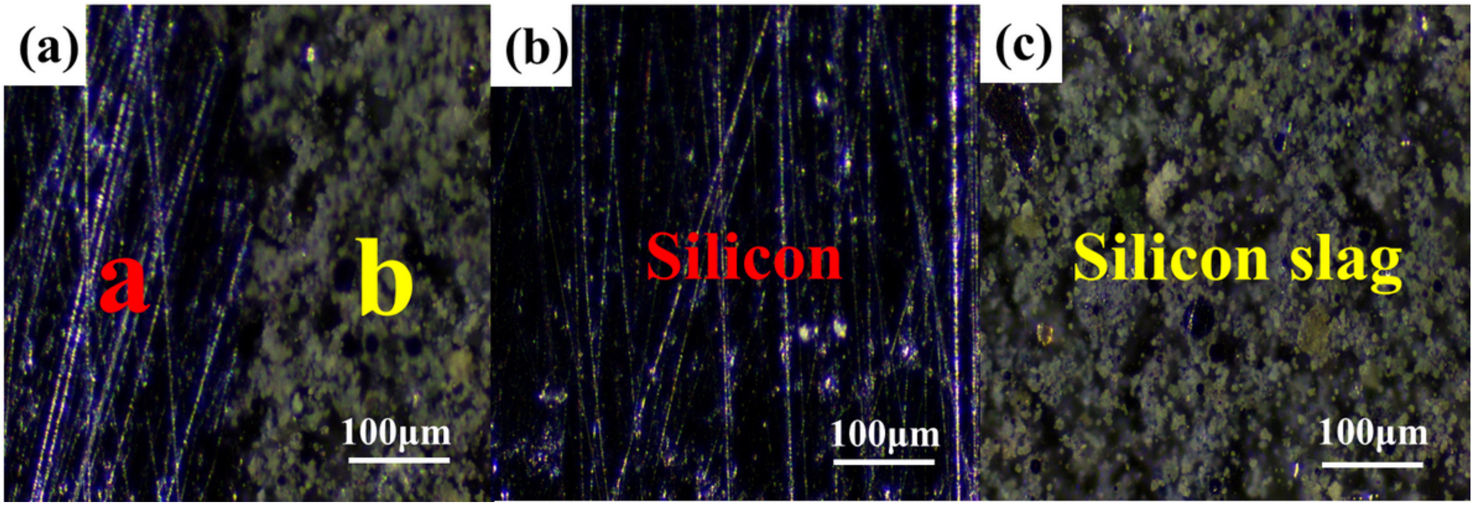

Figure 3

The microscope images for Polished silicon slag. (a) Silicon slag interface(b) Silicon; (c) Silicon Slag.

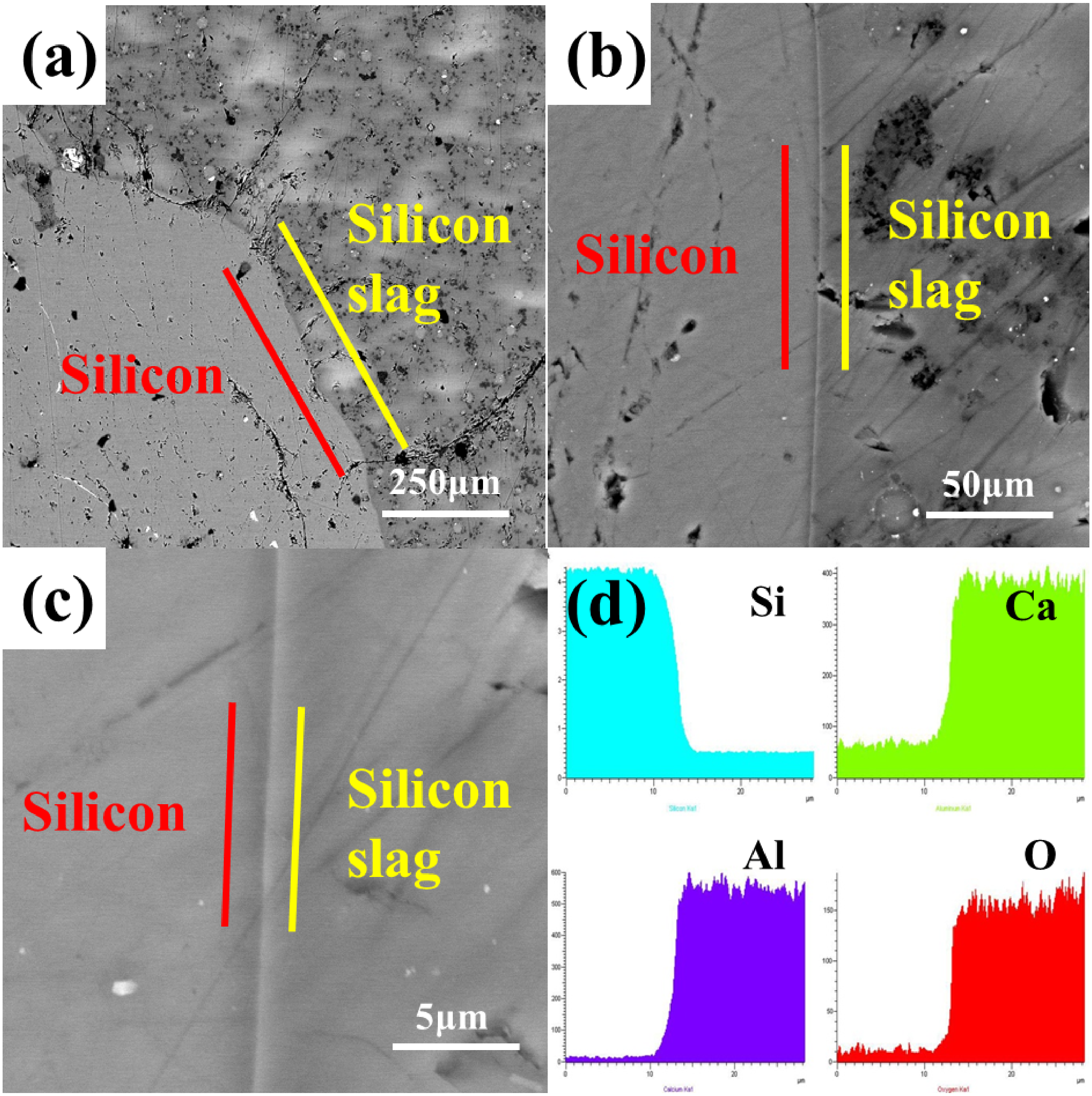

Figure 4

Different magnification for BSEM images. (a) 100x; (b)1000x; (c) 5000x; and (d) the line scan of silicon/slag phase interface.

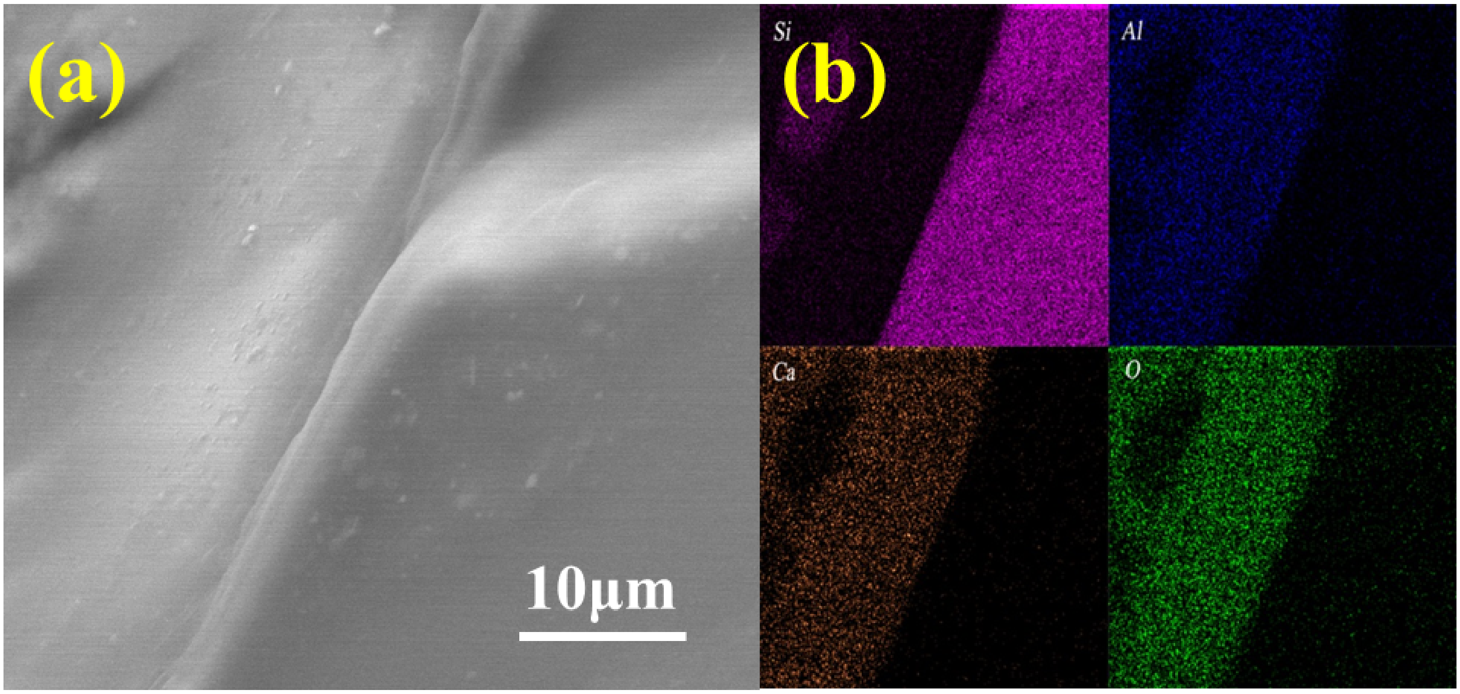

Figure 5

SEM images and EDS elemental mapping of silicon/slag phase interface

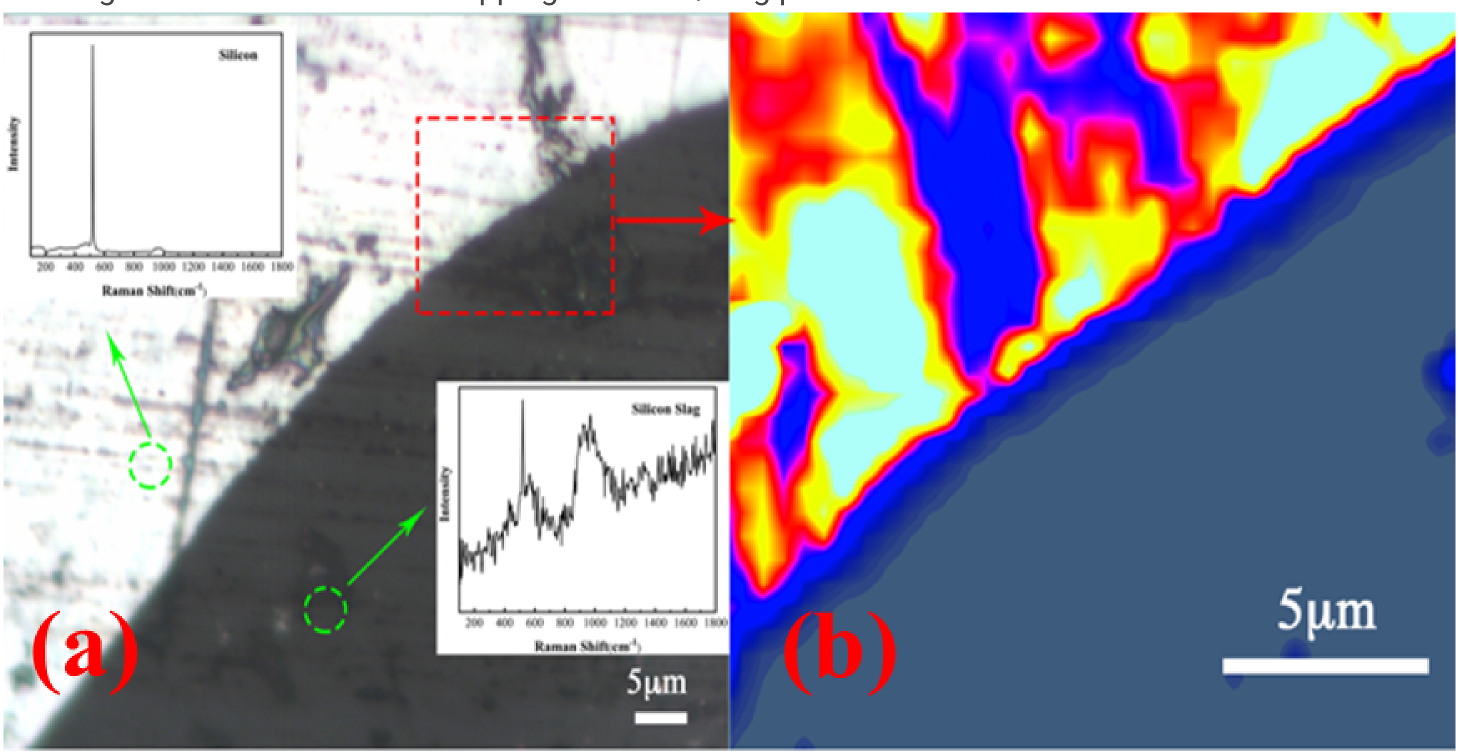

Figure 6

Raman images and EDS elemental mapping of silicon/slag phase interface mapping analysis

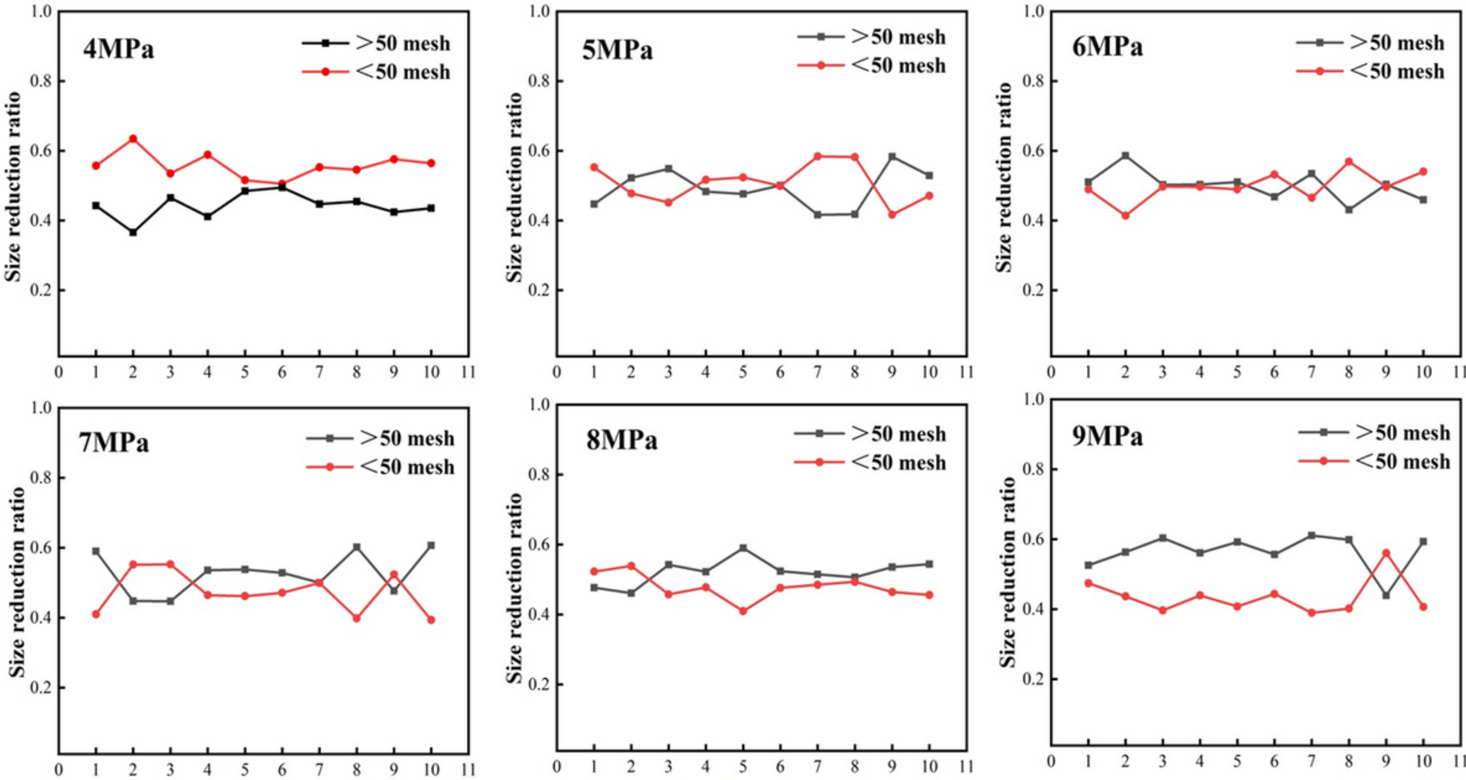

Figure 7

The degree of silicon slag comminution under different pressure.

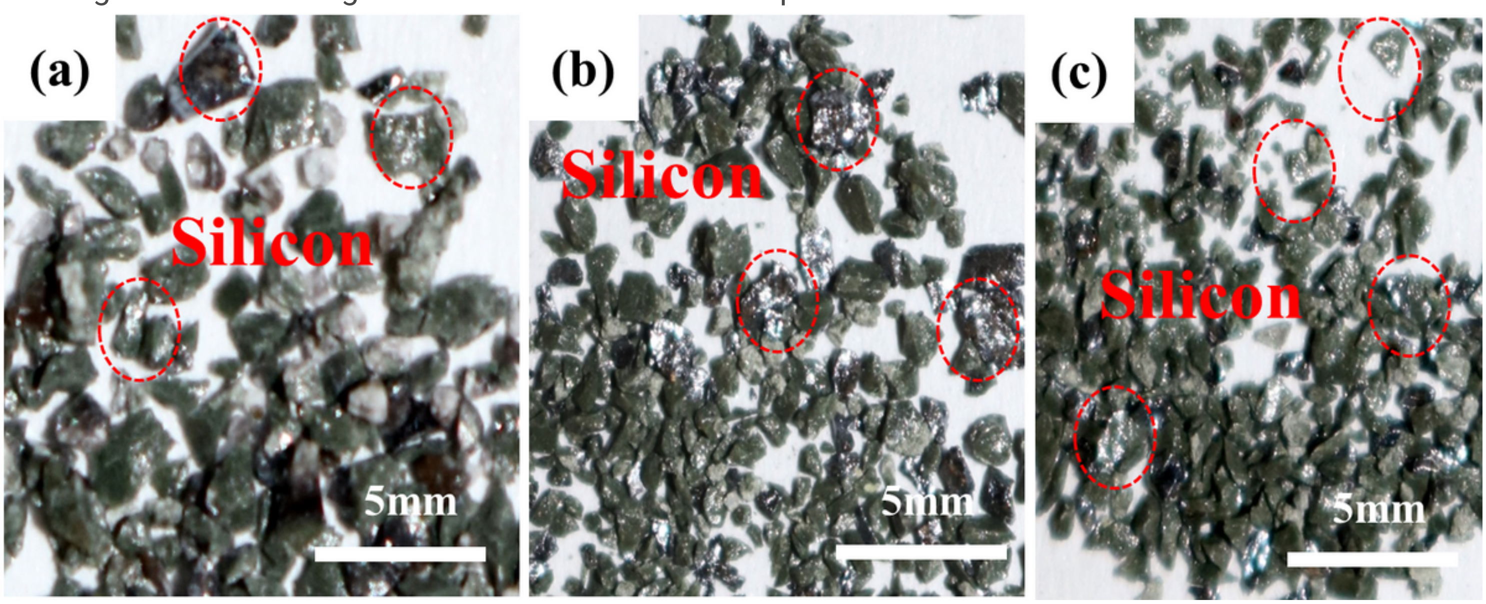

Figure 8

The crushing condition of silicon slag under different pressure. (a) 4MPa; (b) 6MPa; (c) 8MPa

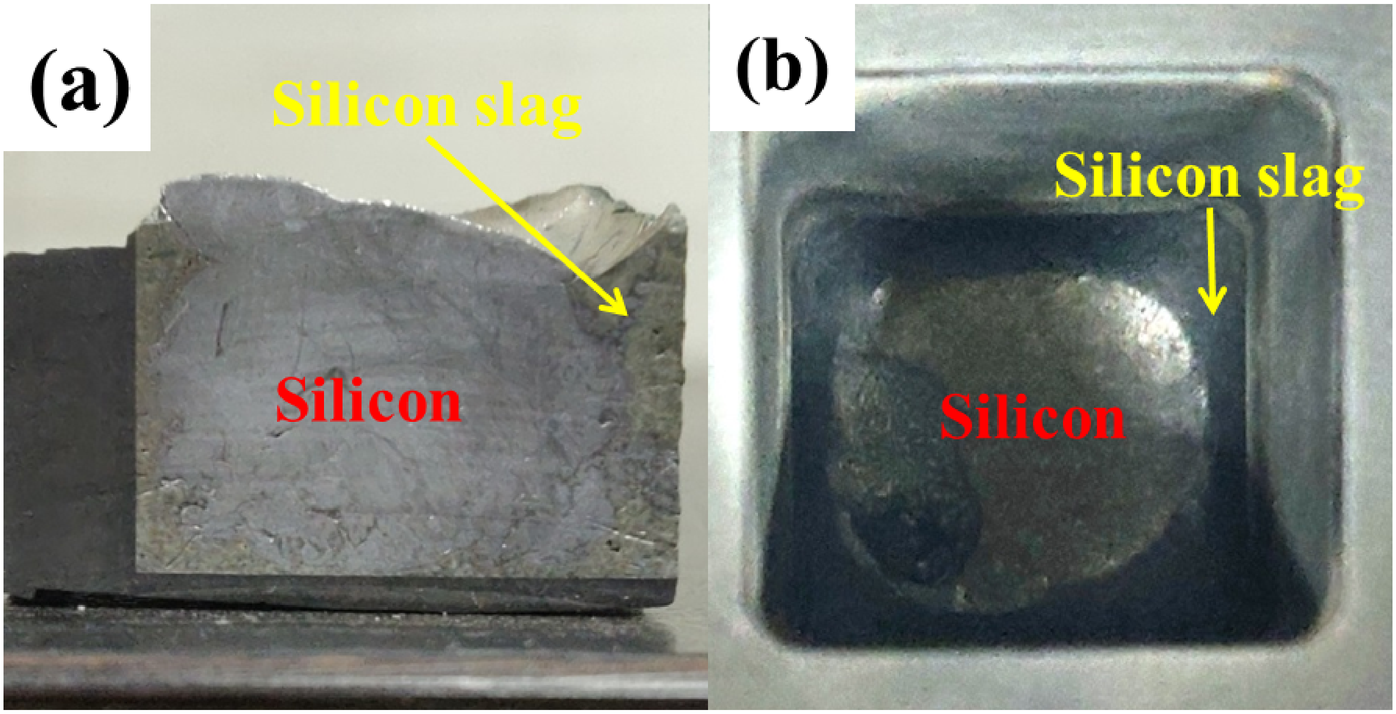

Figure 9

High temperature melting of (a) silicon slag; (b) silicon

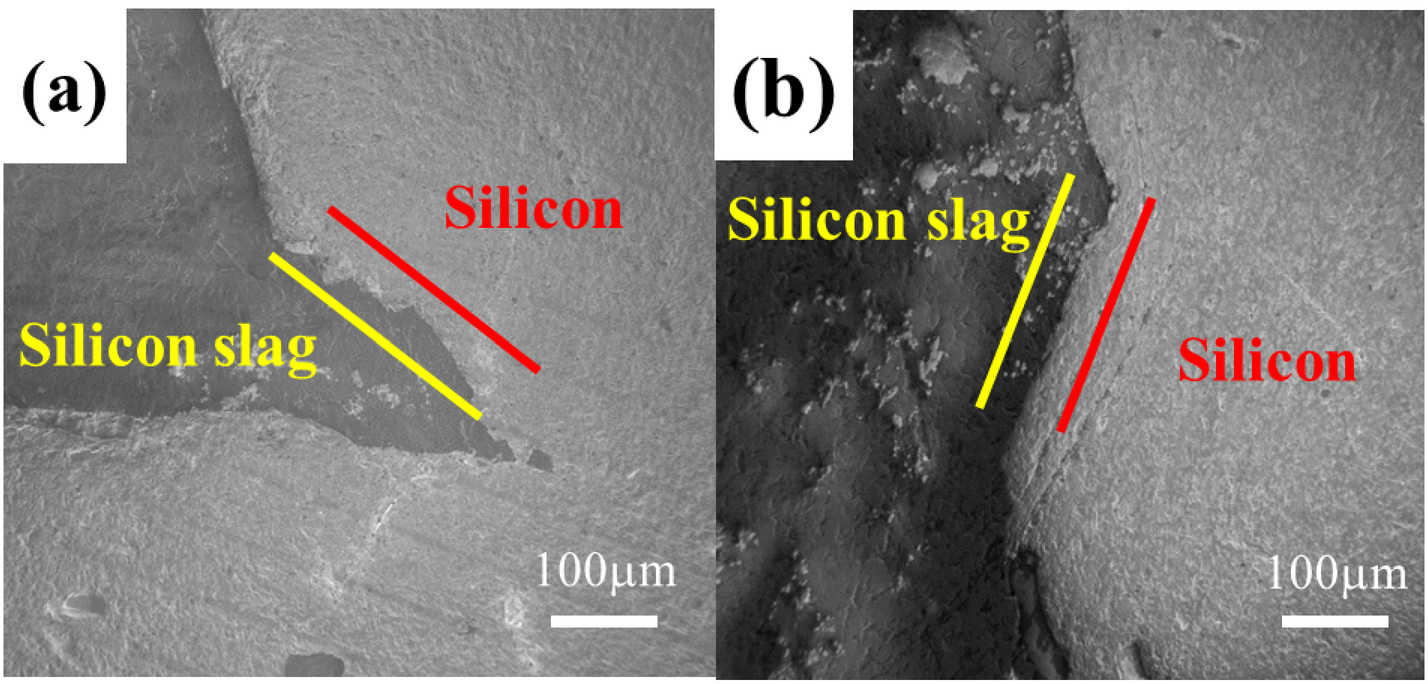

Figure 10

(a) Reconstituted silicon slag and (b) original silicon slag section contrast