Research on the Mechanism Model of Carbon Composite Material Damaged by Erosion in the Thermal Field of Single Crystal Silicon Furnace

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Abstract. Aiming at the problem of the short service life of the carbon/carbon pot wall caused by continuous silicification during the pulling process of single crystal silicon, the paper analyzes the failure mode of the carbon/carbon pot wall and analyzes the influence of the pot wall in the single crystal silicon furnace thermal field. The mechanism of erosion damage. It is concluded from the use situation that the carbon/carbon composite crucible can be used in the field of Czochralski single crystal silicon, and its performance is far better than that of the graphite crucible, and the destruction mechanism of the carbon/carbon composite crucible is analyzed, and solutions are proposed. Through the analysis of the entire industry, carbon/carbon composite crucibles will replace graphite crucibles and become the preferred material for the thermal field of Czochralski silicon single crystals in the future.

Keywords. Carbon/carbon composite crucible, Czochralski single crystal furnace, thermal field system, production process; failure mechanism.

1. Introduction

After more than 40 years of research, the C/C composite materials used in China's engineering applications have broken through the series of key technologies such as high density, high performance, high functionality and large size, and achieved leapfrog development, satisfying aerospace, aviation, photovoltaic, powder metallurgy, The demand for major equipment in areas such as industrial high-temperature furnaces has enhanced China's independent support capabilities for C/C composite materials. In the actual production process of crystalline silicon materials, due to the high temperature, the quartz crucible used to hold the silicon material and the molten silicon material will volatilize to produce a large amount of SiO₂ and Si vapor, which are in contact with the carbon-based thermal field material. At times, oxidation reaction and solicitation reaction are prone to produce corrosion. This corrosion will cause serious damage to the material, thereby affecting the stability of the thermal field,
and at the same time causing safety hazards to the equipment. Therefore, it is of great practical significance to study the corrosion behaviour of carbon materials in the thermal field of crystalline silicon furnaces.

In the field of solar photovoltaics, with the rapid development of monocrystalline silicon Czochralski furnaces, the size of its thermal field structure has been continuously upgraded and expanded. The carbon/carbon composite material pot top, outer guide tube, heater, insulation tube, inner support tube and tight Thermal field components such as firmware have been widely used due to their light weight, strong corrosion resistance, long service life, cost-effective advantages and energy-saving effects, etc., and they have been widely used, especially the carbon/carbon composite cladding [1].

2. Analysis of the failure mode of char

2.1. Related theories

The carbon/carbon composite material crucible top is one of the core thermal field components in the single crystal silicon Czochralski furnace. During the preparation of the silicon single crystal, the carbon-carbon crucible is adjacent to the quartz crucible containing the silicon material and the silicon material inside. During the heating process, the quartz crucible and the molten silicon material release a large amount of SiO$_2$ and silicon vapor. When these gases are in contact with the carbon/carbon crucible top, oxidation reactions and solicitation reactions are prone to cause corrosion. Because the oxygen content in the system is very small, the oxidation reaction can basically be ignored, but the silicification erosion cannot be completely eradicated, and the accumulation of erosion to a certain extent will cause the crucible to fail. As a result, the longer the service life of the charcoal/carbon cup, the lower the operating cost of the equipment for a single furnace, and the safety hazards of the equipment are greatly reduced. Therefore, how to extend the service life through the preparation process of the cup is of extremely important practical significance [2].

Studies have shown that during the operation of the monocrystalline silicon Czochralski furnace, since the melting point of the polycrystalline silicon material is about 1410°C, in order to fully melt the polycrystalline silicon material, the melt temperature must be above 1410°C. At the same time, in order to ensure that the quartz crucible is not melted, the temperature of the quartz crucible cannot be higher than 1720°C. In this temperature range, the reactions of Si, SiO$_2$ and C are as follows:

\[
\begin{align*}
SiO_2 + C & \rightarrow SiO + CO \quad (1) \\
SiO + C & \rightarrow Si + CO \quad (2) \\
SiO_2 + C & \rightarrow SiO + CO \quad (3) \\
Si + C & \rightarrow SiC \quad (4)
\end{align*}
\]

The initial reaction temperature of reaction formulas (1) and (2) is 1150°C, and the initial reaction temperature of reaction formula (3) is 1500°C. At the same time, according to thermodynamic calculations, reaction formula (4) can be reached within the range of R.T.-1720°C, so at the crystal pulling temperature of single crystal silicon Czochralski furnace, silicon vapor can smoothly react with carbon to form SiC. Carbon/carbon composite materials are mainly composed of carbon fibre and matrix carbon, and the corrosion resistance of the two components is quite different. The density of carbon fibre is as high as 1.79g/cm$^3$, and the resistance to solicitation is strong. The reaction of carbon fibre and silicon vapor is mainly the peeling phenomenon caused by the mismatch of thermal expansion coefficient during the silicification process, as shown in Figure 1.
Figure 1. The morphology of carbon fibre after silicification and erosion

As a kind of matrix carbon, resin carbon is a low-density carbon material with multiple closed-cell structure. Its average density is 1.37g/cm$^3$, porosity is as high as 19.5%, and corrosion resistance is poor. The pores and cracks formed after the silicification and erosion of the resin carbon further provide a channel for the propagation of silicon vapor, which intensifies the erosion of the material, as shown in Figure 2.

Figure 2. Morphology of resin carbon after siliconization and erosion

As the solicitation corrosion continues to intensify, the carbon/carbon pot top gradually transforms from the inner surface to the brittle silicon carbide. Inside the carbon/carbon crucible eroded by silicification, the thermal expansion coefficient between the inner surface silicon carbide layer and the matrix carbon/carbon layer is relatively large (SiC thermal expansion coefficient 4.5×10$^{-6}$K$^{-1}$, carbon/carbon composite thermal expansion coefficient 1×10$^{-6}$K$^{-1}$), during repeated heating and cooling processes, thermal stress will be generated inside the crucible, when the thermal stress exceeds the strength of the carbon/carbon composite body, it will crack, and the generation of microcracks will provide a channel for subsequent silicon vapor infiltration, Further intensified the erosion of the inner pot. When the microcracks continue to occur and expand to a certain extent, under the stress of the molten silicon material and the hard impact during charging and discharging, the carbon/carbon crucible
top will produce through cracks that penetrate the entire wall thickness or large area dropouts [3]. Cannot continue to use, as shown in Figure 3.

Figure 3. Carbon/carbon composite crucible failure morphology

From the analysis of the damage mechanism of the above-mentioned carbon/carbon cup top, slowing down the diffusion rate of silicon vapor into the carbon/carbon cup top and increasing the mechanical strength of the cup top can effectively extend the service life of the carbon/carbon cup top. Combining the production process of carbon/carbon composite materials, it is planned to start from the three influencing factors of carbon/carbon composite material density, hoop carbon fibre content (the percentage of hoop carbon fibre content in the total carbon fibre content), and coating. The influence of various influencing factors on the service life of the charcoal/carbon pot [4].

2.2. Gaussian heat source

Studies have shown that the charged particles in the instantaneous discharge channel act on the electrode surface, and its density distribution conforms to the Gaussian distribution, that is, the density of charged particles in the centre of the discharge channel is the highest, and the density of charged particles at the edge is the lowest. The mathematical expression of Gaussian heat source is

\[ q(r) = q_m \exp \left( -k \frac{r^2}{R^2(t)} \right) \]  

(5)

In the formula, \( q(r) \) is the heat flux density at radius \( r \), \( W/m^2 \); \( q_m \) is the maximum heat flux density, \( W/m^2 \); \( k \) is the energy concentration coefficient; \( R(t) \) is the discharge channel radius at time \( t \), m. Because the energy is concentrated during discharge, the discharge area is small, and the Gaussian distribution curve approaches zero at infinity, so in the discharge channel, when \( q(r)<0.05q_m \), the energy can be ignored. Can get

\[ q\left( t \right) = 0.05q_m \]  

(6)

When \( r=R(t) \), from equation (6) we can get

\[ q\left( r \right) = \frac{3}{\pi R^2\left( t \right)} \eta U I \exp \left( \frac{-3r^2}{R^2 \left( t \right)} \right) \]  

(7)

In the formula, \( \eta \) is the energy distribution coefficient; \( U \) is the discharge voltage, \( V \).
3. Experimental Design

3.1. Preparation of the crucible top preform
Choose Japanese Toray 700-12K carbon fibre, first cut the long fibre into short fibres of 3—10mm, and prepare the mesh through the carding machine. The carbon fibre is woven into plain carbon cloth at an angle of 90 degrees, and finally the carbon cloth Alternately laminated with mesh tires are needle punched to form a crucible top preform that meets the requirements of shape, size and density. To densify the preform, first use the chemical vapor infiltration process to densify the crucible top; after the crucible top has a certain strength, use the furan resin impregnation carbonization process for densification. In order to obtain a higher density, it needs to be done multiple times Resin impregnated carbonization treatment to increase the density of the upper pot Finally, after a high temperature purification process of more than 1500%, the final density of the product is greater than 1.509/cm³. The specific parameters are shown in Table 1.

| Carbon materials | Density / (g·cm⁻³) | Flexural strength / Mpa | Compressive strength / MPa |
|------------------|---------------------|-------------------------|---------------------------|
| Graphite         | 1.8                 | 39.2                    | -                         |
| C/C              | 1.4                 | 78.3                    | -                         |
| RCFF             | 0.18                | 1.5                     | 0.35*                     |

The C/C composite material is composed of carbon fibre and pyrolytic carbon, in which the carbon fibre bundles are interlaced, and because the gaps between the carbon fibres cannot be completely filled with pyrolytic carbon during the production process, the material contains more pores; hard carbon felt It is mainly composed of a disorderly arrangement of short carbon fibres, with less pyrolytic carbon content, and poor fixation of carbon fibres, and messy fibres can be seen on the surface. The material has low density, large pores and extremely high porosity, reaching more than 90%.

3.2. Performance characterization of the pot top

3.2.1 Thermal performance. Use the DIIA02C thermal expansion tester to test the linear expansion coefficient according to GB4339-84, the test temperature is room temperature -800°C, and the sample size is 6mm×25mm. The thermal diffusivity and specific heat capacity were tested by NETZS LFA457 thermal constant tester according to the GJB201-1-93 standard, and the thermal conductivity was calculated. The test temperature was room temperature-800°C, and the sample size was 12.75mm×3.1mm.

3.2.2 Mechanical properties and ash content. On the DSS-10T-S electronic universal testing machine, the prepared carbon and carbon composite material were tested for the bending performance in the x-Y direction; the compression performance was tested according to GB 1994-80; the ash content of the material was tested according to YB/T5146-2000.

4. Results and discussion

4.1. The influence of density on the service life of charcoal
Figure 4 shows the trend graph of the average service life of different density carbon/carbon composite crucibles. It can be seen from the figure that as the density increases, the service life of the crucible increases significantly. This is mainly because as the density increases, the carbon/carbon composite material the open porosity of the composite material gradually decreases [5].
Figure 4. The service life of different densities carbon/carbon pot

It can be seen from Figure 4 that the higher-density carbon/charcoal top can effectively slow down the corrosion of silicon vapor entering the material during use. In addition, with the increase in density, the mechanical properties of the carbon/charcoal cup top body also improve. After the solicitation corrosion occurs on the inner surface of the cup top, the strength of the external uneroded part of the carbon/carbon cup top body can completely resist the molten silicon solution. The hoop stress slows down the formation process of penetration cracks, thereby prolonging the service life of the charcoal/carbon pot.

The effect of corrosion parameters on solicitation corrosion the surface micromorphology of carbon materials after corrosion at 1400, 1500 and 1600°C for 5h. As the corrosion temperature increases, the overall density of the graphite surface gradually increases, but the surface micro-cracks gradually increase, and the crack width gradually increases from 0.5 μm to 3 μm. These cracks will cause the decrease of the mechanical properties of the graphite material and reduce its service life. The surface density of C/C composite materials has also gradually increased. The SiC particles on the surface of carbon matrix and carbon fibre have gradually increased, and the peeling phenomenon of carbon fibre and carbon matrix has also increased significantly, and the splitting phenomenon of carbon fibre surface has become more and more serious, showing pulverization. Trend; the surface of hard carbon felt gradually becomes "virtual", the gaps between the internal fibres are filled with a large number of SiC nanowires, the SiC particles on the surface of the carbon fibre gradually increase, the number of nanowires between the fibres increases, and the carbon fibre fragmentation phenomenon getting more serious.

Figure 5. Corrosion depth of carbon materials at different temperatures
Figure 5 shows the diffusion depth of silicon in the material at different temperatures (corrosion time is 5h). It can be seen from the figure that due to the density of the material and the inconsistency of the material composition, the corrosion depth of silicon is obviously different. Graphite has the lowest corrosion depth due to low porosity and mostly closed pores; C/C composite materials have more pores inside, and their corrosion depth is greater than graphite; while hard carbon felt materials have an internal porosity of 90%, the pores are interconnected, providing a channel for the diffusion of silicon vapor, and its corrosion depth is much greater than that of graphite and C/C composites. In addition, the diffusion depth of silicon in graphite and C/C composites increases first and then decreases with the increase in temperature, reaching the maximum at 1500°C, which is about 950μm and 960μm, respectively; while hard carbon felt materials have an obvious increasing trend in materials, and the diffusion depth of silicon element far exceeds that of graphite and C/C composite materials. When the temperature reaches 1600°C, the diffusion depth of silicon element in the hard carbon felt reaches 5mm, which exceeds the thickness of the test material. The corrosion is extremely serious.

**Figure 6. Saturated vapor pressure curve of silicon at different temperatures**

As the temperature increases, the saturated vapor pressure of silicon gradually increases (as shown in Figure 6), resulting in an increase in the amount of silicon vapor, and a corresponding increase in the diffusion rate of silicon, and the concentration of reactive gas accumulated on the surface of the substrate material is also higher. High makes the silicon vapor fully contact the carbon source and accelerates the reaction rate, thereby rapidly forming a relatively dense SiC layer on the surface of the base carbon material. Therefore, as the temperature increases, the density of the SiC layer on the surface of the material gradually increases. The diffusion of silicon in carbon materials mainly includes two ways: the gas diffusion process relying on material pores and defects and the solid diffusion process in the material. The resulting dense SiC layer will hinder the diffusion of silicon vapor into the material to a certain extent, so that the diffusion of silicon will gradually change from gas diffusion to solid diffusion. Although increasing the temperature will promote the diffusion rate of silicon in the solid, it is comprehensive in terms of its diffusion rate will still be greatly reduced. Under the corrosion condition of 1600°C, due to the high temperature, a dense SiC layer is quickly formed on the surface of graphite and C/C composite materials, which hinders the subsequent diffusion of silicon vapor, thus reducing the corrosion depth; while the hard carbon felt is due to pores. The SiC layer formed on the surface cannot form a dense layer, and the diffusion of silicon in its interior is always dominated by gas diffusion, resulting in the continuous increase of the corrosion depth of silicon [6].
5. Related suggestions
In response to the above-mentioned situations in use, Jinbo Technology Co., Ltd. proposed a plan for surface treatment of the crucible surface. The coating is mainly applied to the surface of the C/C composite crucible, and SiC single-phase or composite coating can be generated on the surface of the crucible according to requirements. The reasons for choosing SiC coating are: (1) The hardness of SiC is very high, with a microhardness of 334MaP, second only to diamond, which can significantly improve the wear resistance of the crucible surface and increase the service life of the crucible; (2) the heat of SiC has high conductivity, excellent high temperature strength and high temperature creep resistance. The high temperature bending strength of hot-pressed silicon carbide material at 160 °C is basically the same as room temperature; it has good thermal shock resistance and high chemical stability; at the same time, it can have good thermal expansion compatibility with carbon matrix. (3) SiC high temperature coating material is currently the most studied and developed single-layer anti-oxidation coating system with mature technology. To sum up, the coating can not only improve the wear resistance of the surface of the pot, but also prevent the oxidation and erosion of the oxidizing gas on the surface of the pot at high temperature, improve the service life of the crucible, and at the same time improve the high temperature strength and heat resistance of the crucible Seismic performance, etc.

6. Conclusion
The silicification and corrosion reaction of carbon/carbon composite material and silicon vapor in the thermal field of monocrystalline silicon Czochralski furnace is very easy to occur. During long-term use, the failure mode of carbon/carbon crucible top is caused by the thermal expansion mismatch of the body material from the inside to the outside. Micro-cracks are produced. After the micro-cracks are continuously produced and expanded, they will cause penetrating cracks or local area dropouts during the stress of molten silicon liquid and repeated disassembly and assembly of materials.

References
[1] Deng, Y. Jiao, K., Liu, Z., Zhang, J., & Song, Q. Effects of coke ash on erosion of carbon composite brick. ISIJ international, 59(3) (2019) 412-420.
[2] Qin, F. Peng, L. N., Li, J., & He, G. Q. Numerical simulations of multiscale ablation of carbon/carbon throat with morphology effects. Aiaa Journal, 55(10) (2017) 1-10.
[3] Sanderman, J. & Berhe, A. A. Biogeochemistry: the soil carbon erosion paradox. Nature Climate Change, 7(5) (2017) 317-319.
[4] Liu, Y. Pei, J. Q., Li, J., & He, G. Q. Ablation characteristics of a 4d carbon/carbon composite under a high flux of combustion products with a high content of particulate alumina in a solid rocket motor. New Carbon Materials, 32(2) (2017) 143-150.
[5] Ritchie, J. C. & Rasmussen, P. E. Application of 137cesium to estimate erosion rates for understanding soil carbon loss on long-term experiments at pendleton, oregon. Land Degradation & Development, 11(1) (2015) 75-81.
[6] Kaundal, & Ritesh. Role of process variables on solid particle erosion of polymer composites: a critical review. Silicon, 9(2) (2017) 223-238.