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Journal of the European Ceramic Society 27 (2007) 861–865

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Oxidation treatments for SiC particles and its compatibility with glass

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Abstract

Different thermal treatments were performed to produce a protective coating on the surface of SiC particles in order to allow their incorporation in a glass matrix. These oxidation treatments were carried out in air at different temperatures ranging from 800 °C to 1500 °C and different times at 1200 °C (10 min–48 h). The oxidation kinetics followed the Deal–Grove model and the thickness of the protective coating increased with temperature and SiC particle size. Protected SiC particles with different particle sizes were incorporated in a borosilicate glass. With small particles sizes foam glasses were obtained, whereas particles with higher grain size, i.e., higher coating thickness, were stable in the glass matrix and a smooth glass was obtained.

Keywords: Oxidation; SiC

1. Introduction

Microelectronic devices and sensors with high thermal operation limits are nowadays requested by several industries. In fact, electronic devices working in extreme environments will enable to achieve advances in a number of industries, especially in clean technologies.[1] However, numerous technological challenges need to be addressed for the fabrication of devices working in hard conditions.

The physical and electronic properties of SiC make it a good semiconductor material for high temperature, radiation resistant and high power electronic devices due to its wide energy band gap, high breakdown electric field, high thermal conductivity and high saturated electron drift velocity.[2] On the other hand, microelectronic packaging needs the use of glasses for sealing. The adequate glass must be electrically insulating, thermally stable and ideally non-reacting with SiC substrate, but the stability of glasses with SiC is nowadays under study.[1]

However, it is well known that one of the applications of SiC is as a foaming agent in glasses because SiC reacts with the available oxygen in glasses forming Si, SiO, SiO_2, CO and/or CO_2 and those gases create blisters and bubbles.[3,4]

To avoid the reaction between SiC and glasses and the consequent bubbling a protective barrier must be formed on the SiC particles surface. The main role of these protective coatings is to act as a diffusion barrier to prevent the reaction between the glass and the unprotected SiC particles avoiding further attack. If this is not so, gaseous species (Si, SiO, SiO_2 and CO or CO_2) would be released after oxidation of SiC by atomic or molecular oxygen. Even if no oxygen is introduced in the furnace, the SiC can react with the SiO_2 present in the glass matrix to form gaseous species.[5] Moreover, the formation of a SiO_2 layer should favour the contact between the SiC particles and the SiO_2 in the glass promoting their joining.

The easiest way to achieve the protecting barrier is oxidizing SiC and the characteristics of the protective coating will depend on several experimental conditions as atmosphere, temperature and time of the thermal treatment.

As it is well known, the oxidation of SiC is divided into two regimes: the passive oxidation with the formation of a SiO_2 layer on the SiC surface, according to Eq. (1), and the active oxidation, at higher temperatures, with the vaporization of $SiO_{(g)}$ and $CO_{(g)}$, according to Eq. (2).

$$SiC_{(s)} + \tfrac{3}{2}O_{2(g)} \rightarrow SiO_2 + CO_{(g)} \qquad (1)$$

$$SiC_{(s)} + O_{2(g)} \rightarrow SiO_{(g)} + CO_{(g)} \qquad (2)$$

The transition between these two regimes depends on the nature of SiC, the composition, the gas flow, the partial and total pressures and the temperature.[4,6,7] For SiC to be effectively protected

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doi:10.1016/j.jeurceramsoc.2006.04.041

by SiO_2 coatings it is essential that the materials remain in the passive oxidation regime.[8]

The objectives of this work were to study the kinetics and optimal conditions for the formation of a protective barrier on the SiC particles surface and the introduction of these protected SiC particles in a borosilicate glass matrix to evaluate the barrier stability.

2. Experimental procedures

Several SiC powders from Navarro S.A. (Spain) with different particle sizes were selected to evaluate the optimum oxidation thermal treatment prior to the introduction of the protected SiC particles in a borosilicate glass matrix. As-received SiC powders were characterized by means of particle size (Laser Coulter LS130). SiC particles were oxidized in air at temperatures ranging from 800 °C to 1500 °C for 2 h and kinetics studies were performed in air at 1200 °C for times from 10 min to 48 h.

Oxidized and non-oxidized SiC powders were characterized by means of X-ray diffraction (Siemens D5000, Cu Kα radiation, 0.02, 2θ/min) and scanning electron microscopy (DSM950 Carl Zeiss).

The borosilicate glass was supplied by Fritta S.L. (Spain). The glass powder was mixed with 3 wt% SiC by stirring. The slurry (glass matrix and SiC) was applied onto green porcelain tiles and fired at 1190 °C for 15 min. The stability of the SiO_2 coating was evaluated by SEM.

3. Results and discussion

3.1. SiC powder characterization

SiC powders were black and their crystal structure was α-SiC with a mixture of rhombohedral and tetragonal symmetries. The average particle sizes of the different as-received powders are resumed in Table 1.

3.2. Oxidation treatments

When SiC is oxidized to SiO_2 in the passive regime, there is a net weight gain according to Eq. (1), whereas at higher temperatures there is a net weight loss in the active oxidation regime according to Eq. (2). The weight changes as a function of temperature for the different SiC powders are depicted in Fig. 1. The weight gains increased with temperature (up to 1400 °C) and with the decrease of SiC particle size. In this case, the transition between active-to-passive oxidation is at approximately 1400 °C, varying a little with particle size (the smaller particle size the higher transition temperature).

Table 1
Particle sizes of as-received SiC powders

Powder	Average particle size (μm)	$(d_{90} - d_{10})/d_{50}$
N1	140.5	0.78
N2	55.0	0.96
N3	20.7	1.35
N4	3.67	2.46

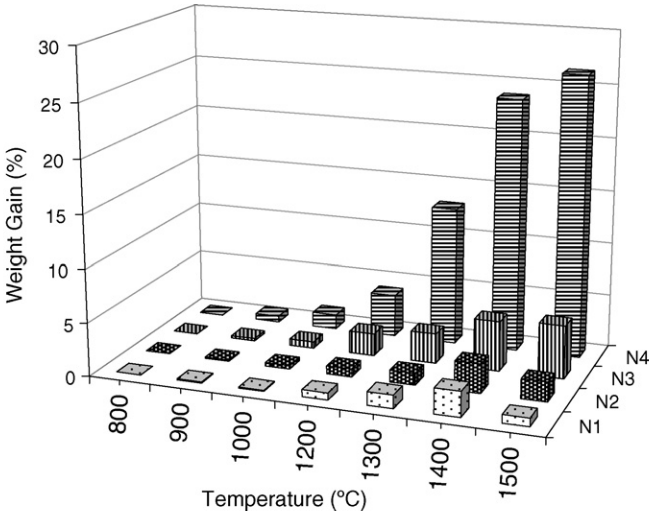

Fig. 1. Weight gains as a function of temperature (2 h) and particle size for the different SiC powders.

The volume fraction of SiO_2 formed on the surface of SiC particles can be calculated from the net weight gains at those temperatures using Eq. (3).[9]

$$V_{SiO_2} = \frac{3\,\Delta w/\rho_{SiO_2}}{((W - 2\,\Delta w)/\rho_{SiC}) + (3\,\Delta w/\rho_{SiO_2})} \tag{3}$$

where W is the initial mass of the as-received SiC powder before thermal treatment, Δw the net weight gain after the oxidation treatment and ρ_{SiC} and ρ_{SiO_2} are the densities of SiC (3.21 g/cm^3) and α-crystobalite SiO_2 (2.27 g/cm^3), respectively.[10]

Assuming that SiC particles are spherical and homogeneous in size, the thickness of the SiO_2 coating formed onto the surface of SiC particles can be calculated from Eq. (4).[9]

$$t = 1.29 r_1 (1 - \sqrt[3]{1 - V_{SiO_2}} \tag{4}$$

where t is the final thickness of the SiO_2 layer, r_1 the initial radius of the SiC particles and V_{SiO_2} is the volume fraction of SiO_2 calculated using Eq. (3).

Fig. 2a shows the evolution of the volume fraction of SiO_2 formed as a function of temperature calculated from Eq. (3) and Fig. 2b shows the thickness of the SiO_2 layer as a function of temperature calculated from Eq. (4). As it is shown, the thickness of the SiO_2 coating increased with particle size (N1). At $T > 1400$ °C there is a decrease of the SiO_2 layer thickness because oxidation entered in the active regime (Eq. (2)).

The SiO_2 layer formation was evaluated by XRD and the results are shown in Fig. 3. The X-ray analysis identified the major SiO_2 crystalline phase at all temperatures as α-crystobalite. As it can be seen, the (1 0 1) α-crystobalite diffraction peak ($2\theta = 22.15°$) increased with temperature, whereas the (1 1 1) SiC diffraction peak ($2\theta = 35.65°$) decreased. Table 2 resumes the increase of the XRD diffraction peak as a function of oxidation temperature.

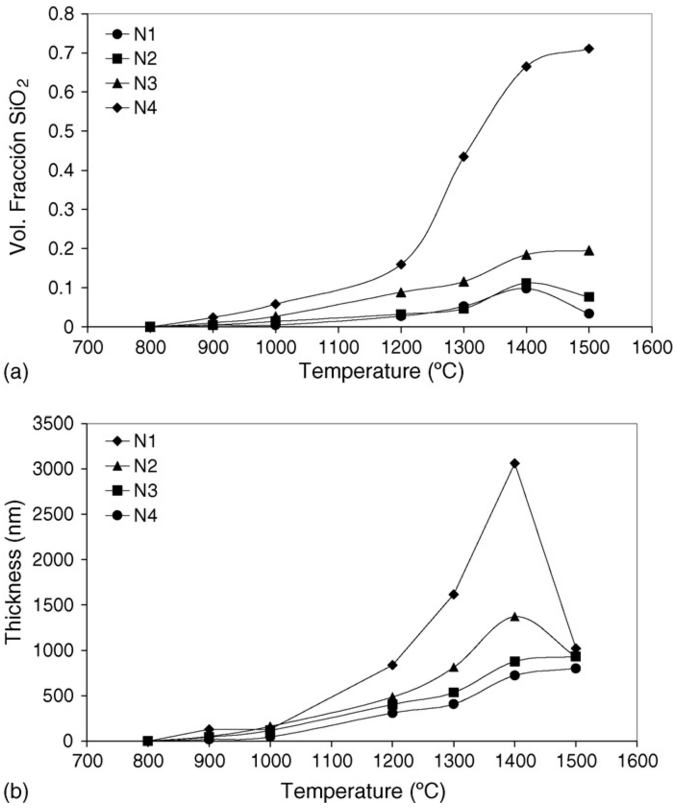

Fig. 2. (a) Volume fraction of SiO_2 as a function of temperature (2 h) and particle size calculated from Eq. (3). (b) Thickness of the SiO_2 layer as a function of temperature and particle size calculated from Eq. (4).

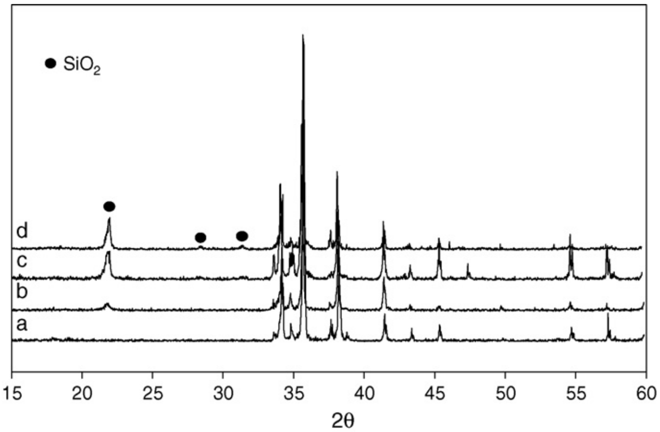

Fig. 3. XRD patterns of N1-SiC powders: (a) as-received, (b) 1200 °C, (c) 1300 °C and (d) 1400 °C (soaking time 2 h).

Table 2
Relative increase (%) of (1 0 1) diffraction peak of SiO_2 as a function of temperature for N1 powders

Temperature (°C)–2 h	$I_{(hkl)}\mathrm{SiO_2}/(I_{(hkl)}\mathrm{SiO_2}+I_{(hkl)}\mathrm{SiC})$
As received	0.32
1200	2.89
1300	13.41
1400	26.14

3.3. Oxidation kinetics

The kinetics of the oxidation treatments was evaluated on N4-SiC powders at 1200 °C for times ranging from 10 min to 48 h. The kinetics of SiC oxidation is usually described by the Deal–Grove diffusion-reaction model,[11] described by Eq. (5).

$$X^2 + AX = Bt \tag{5}$$

where X is the thickness of the oxide coating, t the time, B the parabolic rate constant and B/A is the linear rate constant.

This model considers two sequential processes as rate controlling: interfacial reaction at the SiC–SiO_2 interface, rate controlling at short times and oxygen transport across the layer, rate controlling at long times. In general, passive oxidation of SiC is thought to be kinetically controlled by diffusion of molecular or atomic oxygen through the silica layer.[12] According to this model, for short oxidation times

$$X \approx \frac{B}{A}t \tag{6}$$

and for relatively long oxidation times

$$X^2 \approx Bt \tag{7}$$

Fig. 4a shows the application of the Deal–Grove model to the oxidation of N4-SiC powders at 1200 °C. The parabolic rate con-

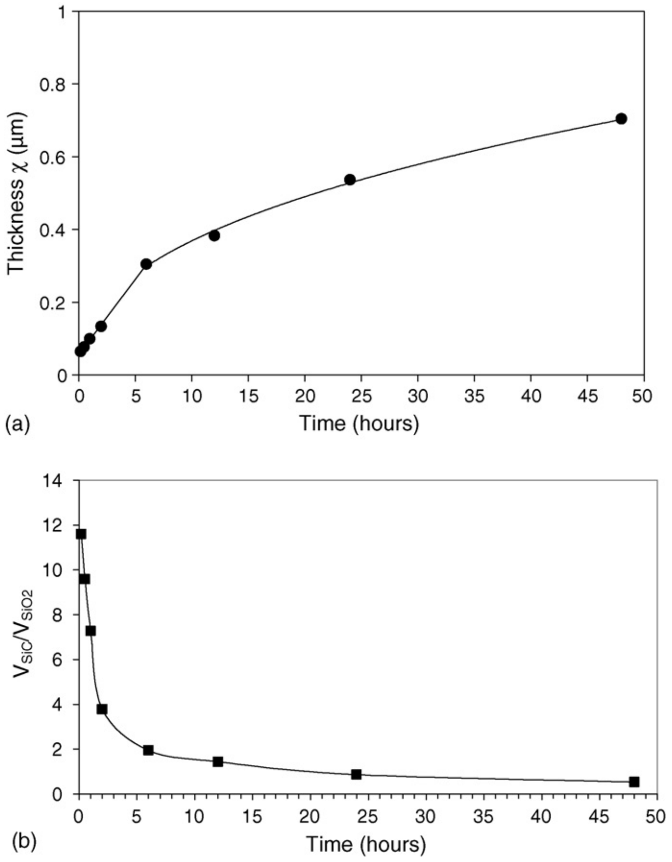

Fig. 4. (a) Deal–Grove model for the kinetics of the oxidation of N4-SiC powders at 1200 °C and $P_{O_2} = 0.22$ atm. (b) V_{SiC}/V_{SiO_2} ratio as a function of time at 1200 °C for N4-SiC powders.

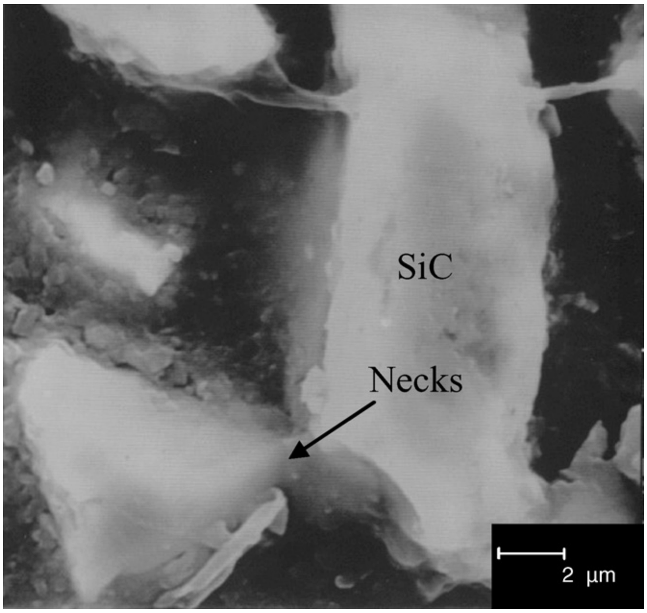

Fig. 5. SEM micrograph of N4-SiC powders oxidized at 1400 °C–2 h showing the formation of necks between the oxidized SiC particles.

stant (B) calculated from the curve was $3.33 \times 10^2\ \mathrm{nm^2/min}$. This value is in good agreement with that obtained by Lamoroux[13] for C/SiC materials. Fig. 4b depicts the decrease of $V_{\mathrm{SiC}}/V_{\mathrm{SiO_2}}$ ratio as a function of time at 1200 °C. As it can be seen, the rate of formation of SiO_2 is high during the first 5 h of treatment, but for times longer than 5 h there were slight changes in the rate of SiO_2 formation. This is an important parameter to choose the duration of the oxidation treatment.

3.4. SEM characterization of oxidized powders

Fig. 5 shows the SEM micrographs of oxidized N4-SiC powders at 1400 °C–2 h. The SiO_2 protecting layer onto the surface of SiC particles was clearly observed. The formation of necks between SiC-coated particles is also evident. These necks could be responsible for the agglomeration of oxidized powders and several problems during the dispersion of the particles into the glass matrix could appear.

3.5. Interaction between SiO_2-coated SiC particles and glass matrix

In Fig. 6 the external aspect of the different glasses (N1–N4-SiC glass) can be seen. As it is shown, particle size of SiC powders had a tremendous influence on the foaming of the glass. In fact, N1- and N2-SiC glasses (SiC particles oxidized at 1400 °C–2 h), with higher particle size and higher thickness of SiO_2 coating, showed a smooth surface with no bubbling. On the contrary, N3 and N4 glasses (SiC particles oxidized at 1400 °C–2 h) showed a very rough surface in which foaming is clear. These results indicate that in the former powders (N1 and N2) the SiO_2 layer is acting as a diffusion barrier avoiding the reaction between the glass matrix and the SiC particles and, therefore, the bubbles formation. On the other hand, the SiO_2 coating in N3- and N4-SiC powders is not thick enough to protect the SiC particles and a further oxidation of SiC particles is produced within the glass with the subsequent gas evolution (CO and CO_2) and foaming.

Fig. 7 shows the SEM micrographs of oxidized SiC particles embedded in the glass matrix. As it can be seen, the N1-SiC particle is almost completely surrounded by the SiO_2 coating

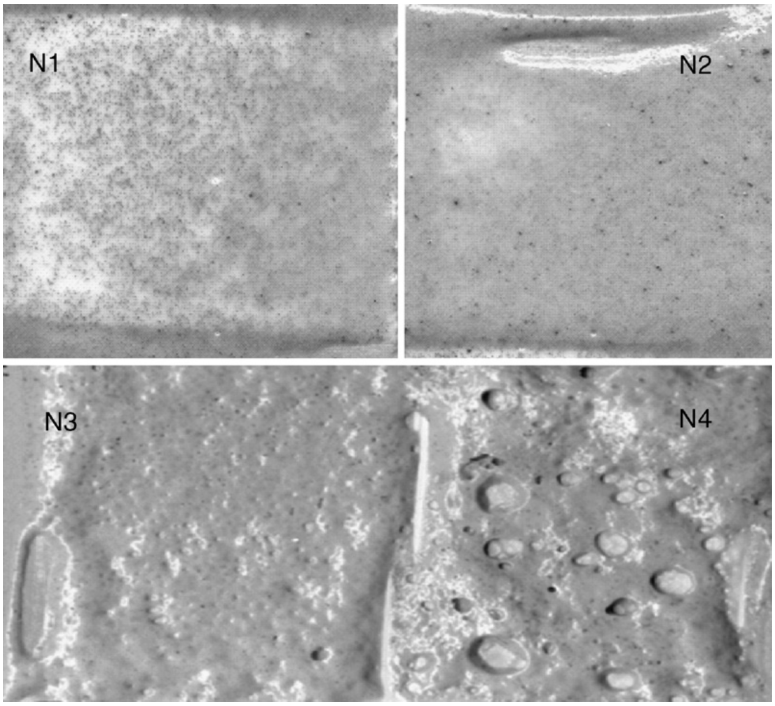

Fig. 6. External aspect of different glass matrixes with N1–N4-SiC powders treated at 1400 °C–2 h. Glass was fused at 1190 °C–15 min.

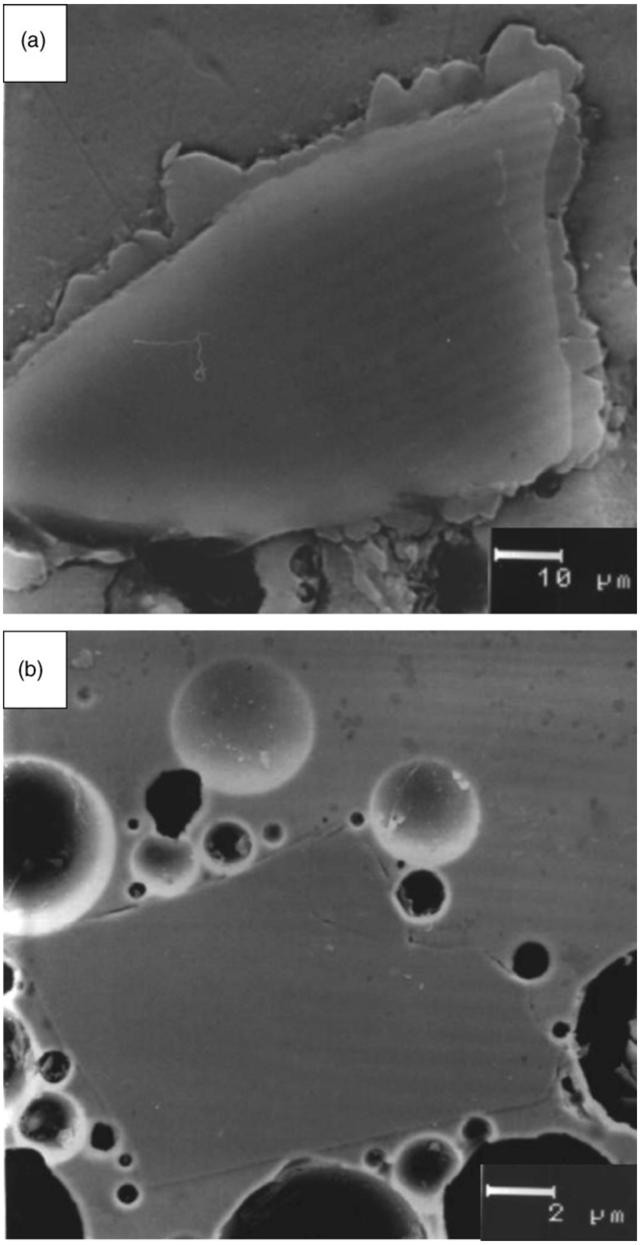

Fig. 7. SEM micrographs of: (a) N1-SiC glass matrix and (b) N4-SiC glass matrix.

and no bubbles formation was observed except for some big ones formed as consequence of an increase of the viscosity of the borosilicate glass near the SiC particles.[14] On the contrary, N4-SiC is not sufficiently protected by the SiO_2 coating and small bubbles completely surrounded SiC particle and subsequent foaming of the glass was produced.

4. Conclusions

The active protection of SiC particles by oxidation treatments strongly depends on temperature and particle size. The kinetics study confirmed the Deal–Grove diffusion-reaction model dependence and that the more efficient treatment is achieved within the first 5 h of thermal treatment. The SiO_2 protective coatings with higher thickness were achieved for N1-SiC powders, those with higher particle size (140 μm), at 1400 °C for 2 h. At temperatures higher than 1400 °C the thickness of the protective layer decreased indicating the entering in the active oxidation regime. The study of the stability of the SiO_2 coating in a glass matrix revealed that in those SiC powders with smaller particle size the thickness of the protective layer is not high enough to protect against the oxidation of SiC particles inside the glass matrix and a number of bubbles were formed with the consequent foaming of the glass. On the contrary, when SiC powders with higher particle size and therefore with a higher thickness of the SiO_2 coating were used the protective layer was stable, there was no bubble formation and, consequently, smooth surface glasses were obtained.

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