Effect of Hydrogen Reduction on Properties of Lead Silicate Glass for Microchannel Plates

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Abstract. Hydrogen reduction process is an important process in the produce of microchannel plates (MCPs). The influence of hydrogen reduction temperature and time on the properties of lead silicate glass and MCPs were investigated by analyzing the spectral transmission, XRD, surface resistivity of the lead silicate glass and electron gain and bulk resistance of MCPs. Results show that the metal crystal of lead has been produced on the surface of glass after hydrogen reduction. With the increase of the reduction temperature or the reduction time, the transmittance and surface resistivity decreases. Meanwhile, the bulk resistance has the same changing trend. The best reduction temperature and time are available for the MCPs prepared by the lead silicate glass.

1. Introduction

Microchannel plates (MCP) with high gain, low noise, high resolution, self-saturation and other characteristics, is a kind of advanced electron multiplier and has important application in many fields, such as night vision, nuclear detection, particle counting, space science and medical treatment [1-3]. Since 1960s, lead silicate glass materials have been the first choice for commercial MCP [4], because of its wide glass forming range, easy melting, high secondary electron emission coefficient and suitable electrical conductivity after hydrogen reduction.

There are some changes in the surface state, composition and properties of lead silicate glass during the process of hydrogen reduction, which is a key and final procedure to determine the performance of MCPs. As we all known, hydrogen reduces the lead ions and bismuth ions in the glass to metal atoms at high temperature, which improves the conductivity of the MCPs. Moreover, the change of surface chemical state and morphology is beneficial to improve the secondary electron yield of lead silicate glass. All of these experimental results show that the hydrogen reduction process has an important effect on the performance of MCPs.

Some recent studies on the surface composition and morphology by different MCPs procedures were carried out in our laboratory. The chemical state of MCPs composition after acid etching and hydrogen reduction was analyzed by XPS [5]. Recently, we have also found the surface nano-scale morphology change of MCPs prepared under different reduced conditions [6-7]. These works have positive effects on revealing the electrical properties of MCPs.

However, there is no much work on the effects of hydrogen reduction on the properties of lead silicate glass and MCPs, especially the direct correspondence between hydrogen reduction and performances of MCPs. This work investigated the changes of performances of glass and MCPs with different hydrogen reduction parameters, in order to provide scientific guidance for optimizing reduction process parameters and improving MCPs’ performance.
2. Experimental
The experimental MCPs were prepared by lead silicate glass with 66% of SiO$_2$, 18% of PbO, 8% of (Na$_2$O+K$_2$O), 5% of (MgO+BaO) and 3% of Bi$_2$O$_3$ as raw material. Glass samples were prepared by using melt quenching method from analytical reagent grade SiO$_2$, Pb$_3$O$_4$, Na$_2$NO$_3$, K$_2$NO$_3$, Ba(NO$_3$)$_2$, Mg$_2$(OH)$_2$CO$_3$, Bi$_2$O$_3$. Well-mixed powders containing appropriate amounts of chemicals were melted in a corundum crucible in air at 1450℃ for 2h, and then the as-quenched glasses were annealed at 500℃ for 5h to remove residual stresses. Then the glass discs with the diameter of 25mm and thickness of 3mm were prepared for performance testing and reduction treatment. What’s more, the glass was also used to prepare MCPs with a 6 μm diameter and 40 ratio of length to diameter.

The glass discs and MCP samples were placed into a high temperature reduction furnace, and treated at various temperature and time. Some samples were reduced under different temperature for 2 hours, another samples were reduced under 500℃ in different time. The reduced samples should be immediately vacuum-packaged after taking out from the reduction furnace.

Spectrophotometer (UV1901PC, Shanghai Phoenix Optical Co., China) was used to measure the spectral transmittance of glass samples before and after reduction in the spectral range of 190-1100 nm, to characterize the reduction degree of the lead silicate glass under different reduction parameters. The crystallization of the glass after reduction is identified by X-ray diffractomer (D8 Advance, Bruker, Germany) with a wavelength of Cu Kα ($\lambda = 1.5406$ Å), in the 2θ range from 10° to 75°, at a scanning speed of 0.02°/min. The surface resistivity are measured using a resistance meter (4339B, Agilent, USA), with conductive rubber as electrode material, and 30N pressure on the electrode and sample, at test voltage of 500 V and electric time for 1 minute. Moreover, the electron gain at 800V and bulk resistance of MCPs was measured by Electrical Performance Test Table for MCPs (China Building Materials Academy, China) [8].

3. Results and Discussion
3.1. Effects of reduction temperature on properties of lead silicate glass and MCPs
The spectral transmission curves of glass samples reduced under different temperature was investigated. As shown in figure 1, the visible light transmittance of the lead silicate glass decreases gradually, with the increase of reduction temperature. Moreover, when the reduction temperature exceeds 500℃, the visible light transmittance of glass is nearly 0.

Figure 1. Spectral transmission curves of glass samples reduced under different temperature

As we known, hydrogen reduces the lead ions and bismuth ions in the glass to metal atoms at high temperature, and that’s reason why visible light transmittance decreases according to the theory of absorption of light by metal atoms [8]. In this experiment, the higher temperature reduces, the greater reduction reaction rate obtains. When the reduction temperature is higher than 500℃, the reaction is already very enough in 2 hours, which means that there are enough metal atoms by reduced to absorb visible light completely.

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In order to investigate the metal atoms during reduction, we used the XRD method to detect metal crystallization on lead silicate glass surface. The results are shown in figure 2, as we can see, the crystals of Pb and Pb-Bi are formed after high temperature reduction above 400°C, while there is no crystalline phases can be separated from parent glasses before reduction. The crystal phase was calibrated with the standard XRD spectrum, and the corresponding crystal plane index of the main peak is shown in the figure. As shown, lead is cubic crystal phase, Fm-3m (225) space group, while Pb-Bi is six square crystal phase and P63/mmc (194) space group. The X diffraction data of (111) crystal plane of lead was selected to calculate the crystalline size by Scherrer formula, as shown in table 1. With the increase of reduction temperature, the crystalline size of lead increases. This is consistent with the results obtained by atomic force microscopy [6].

![XRD patterns of glass surface reduced under different temperature](image)

**Figure 2.** XRD patterns of glass surface reduced under different temperature

| Temperature(℃) | Half peak width(°) | Crystalline size (nm) |
|----------------|--------------------|-----------------------|
| 400            | 0.917              | 89                    |
| 500            | 0.692              | 118                   |
| 600            | 0.673              | 126                   |

**Table 1.** Crystalline size of Lead metal calculated by Scherrer formula

![Surface resistivity of glass samples reduced under different temperature](image)

**Figure 3.** Surface resistivity of glass samples reduced under different temperature

As a result of the increase of metal atoms, the surface resistivity of lead silicate glass will decrease gradually. This has been confirmed by the results of surface resistivity showed in figure 3. The surface resistivity of lead silicate glass decreases rapidly with the increase of reduction temperature, from $7.8 \times 10^{13} \Omega$ to $6.6 \times 10^{10} \Omega$ (500°C). However, the surface resistivity increases slightly, when the
reduction temperature continues to rise to 600℃. This may be due to the volatilization of lead atoms at high temperatures or the distribution of metal crystal has changed [6-7].

Finally, the electron gain and bulk resistance of MCPs were measured respectively, which was shown in figure 4. Clearly, the bulk resistance of MCPs decreases obviously after hydrogen reduction, has a minimum bulk resistance less than 200MΩ under the reduction temperature from 450℃ to 550℃. Meanwhile, the bulk resistance will increase under the reduction temperature of 600℃. However, the change of electron gain is contrary to the bulk resistance, which has the highest gain under the reduction temperature from 400℃ to 550℃.

![Figure 4. The electron gain and bulk resistance of MCPs under different temperature](image)

3.2. Effects of reduction time on properties of lead silicate glass and MCPs

To further analyze the influence of reduction process on the lead silicate glass and MCPs, the samples were reduced at 500℃ in different time. Then the spectral transmission, crystallization on the surface, surface resistivity of the glass and the performance of MCPs were investigated. Finally, we obtained a similar rule of effects between reduction time and properties, as reduction temperature played.

![Figure 5. Spectral transmission curves of glass samples reduced in different time](image)

The spectral transmission curves of glass samples reduced in different time was shown in figure 5. The transmittance of glass decreases rapidly with the prolongation of reduction time. This is because the diffusion of hydrogen in glass is the main factor affecting the reduction reaction at a certain temperature. More metal atoms obtained by prolonging the time. Figure 5 also shows that the chemical reaction between lead silicate glass and hydrogen at 500℃ is very fast.

The XRD patterns of reduced glass samples in different time were shown in figure 6. As shown in figure 6, with the prolongation of reduction time, the diffraction peak width narrows, the surface metal crystallization phenomenon is more obvious, and the metal content increases. More accurately, the
crystalline size of lead metal calculated by Scherrer formula from the XRD data was shown in table 2. The results of the change of surface resistivity of glass samples reduced in different time (see figure 7) also confirms this conclusion, and it is also consistent with other research results [6].

![Figure 6. XRD patterns of glass surface reduced in different time](image)

**Table 2. Crystalline size of Lead metal calculated by Scherrer formula**

| Time/hour | Half peak width/° | Crystalline size /nm |
|-----------|------------------|----------------------|
| 0.5       | 1.146            | 71                   |
| 1.5       | 0.938            | 87                   |
| 2.0       | 0.692            | 118                  |
| 2.5       | 0.658            | 124                  |
| 3.5       | 0.638            | 128                  |

![Figure 7. Surface resistivity of glass samples reduced in different time](image)

In figure 8, the electron gain and bulk resistance of MCPs reduced in different time were measured, and the results show that the MCPs have relatively stable high gain and low resistance after reduced in 1.5 hours or longer.
Figure 8. The electron gain and bulk resistance of MCPs reduced in different time

4. Conclusions
The influence of hydrogen reduction temperature and time on the properties of lead silicate glass and MCPs was investigated. With the increase of reduction temperature or time, the amount of metal atoms on the surface of the glass increases, the crystalline size increases and the transmittance decreases. The reduction process also has important influence on the gain and resistance of MCPs. The best reduction temperature and time are available for the MCPs prepared by the lead silicate glass with 66% of SiO₂, 18% of PbO, 8% of (Na₂O+K₂O), 5% of (MgO+BaO) and 3% of Bi₂O₃ in this work. The optimum temperature is 400-500°C, and the optimal reduction time is 1.5~3 hours.

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