Original Paper

Comparison of metallic silicon inclusions in industrial container glass and laboratory melts

Renate Reisch, Dörte Stachel and Elke Tessmann

Otto-Schott-Institut für Glaschemie, Friedrich-Schiller-Universität, Jena (Germany)

Metallic silicon inclusions in glasses obtained from different container glass companies and from laboratory melts by addition of metallic cuttings (aluminum, magnesium) were examined using light and scanning electron microscopy. The composition of the formed silicon spheres is always similar. The metallic inclusions are composed of silicon with a very small part of finely distributed iron–silicon alloys. In amber and green glass chromium, manganese and copper are additionally enriched as further main elements in these alloying phases. Differences in the composition of silicon spheres are due to the dwell time and the concentration of polyvalent ions in the melt.

Vergleich von metallischen Siliciumeinschlüssen in industriellem Hohlglas und Laborschmelzen

Metallische Siliciumeinschlüsse in Glasproben aus verschiedenen Behälterglasbetrieben und aus Laborschmelzen mit Metallspänen (Aluminium, Magnesium) wurden mit der Licht- und Rasterelektronenmikroskopie untersucht. Die Zusammensetzung der metallischen Einschlüsse ist ähnlich. Die metallischen Siliciumkugeln bestehen aus Silicium mit einem sehr geringen Anteil von feinverteilten Eisen–Silicium-Legierungen. In Braun- und Grünglas reichern sich außerdem Chrom, Mangan und Kupfer als weitere Hauptelemente in diesen Legierungsphasen an. Unterschiede in der Zusammensetzung der Siliciumkugeln werden durch die Verweilzeit und die Konzentration der polyvalenten Ionen in der Schmelze hervorgerufen.

1. Introduction

In general, it is known that in the container glass industry by metallic contaminations of recycled cullet metals enter the furnace and lead to the formation of spheres of elementary silicon in the melt [1 to 4]. The main constituent of the caps, rings, foils and metallic paper is aluminum contaminated by small concentrations of magnesium, iron, manganese, titanium, silicon. The permissible quantity of aluminum impurities in recycled cullet is 5 g/t glass [5].

In industry production losses of 0.01 to 0.5% are attributed to silicon spheres. The metallic inclusions occur more often in flint glass than in green and amber glass. In this paper the results of the examinations of the silicon spheres from the production process and from laboratory melts with added aluminum and magnesium cuttings are presented. Furthermore, it is shown that the composition of silicon spheres obtained from alkali–lime–silica glass is similar. Thus, the metallic inclusions are formed by the same reaction mechanism.

2. Silicon spheres from industrial melts

About 1200 flint glass samples containing metallic silicon spheres from Oberland Glas AG, Bad Wurzach (Germany), Wiegandglas, Großbreitenbach (Germany), Vetropack, Bülach (Switzerland), and Vetropack Austria GmbH, Kremsmünster, were examined comparing appearance, size and composition of the silicon spheres.

2.1 Light microscopy

Using the light microscopes Citoval 2 (Carl Zeiss, Oberkochen (Germany)) and Interphako (Jenapol, Zeiss, Oberkochen (Germany)), the metallic inclusions in container glass were examined. According to their appearance, the silicon spheres were subdivided into three groups:

first group: simple silicon spheres,
second group: silicon spheres with bubbles and,
third group: silicon spheres with stress cracks.

In table 1, the results of a comparison of silicon spheres in samples from different container glass companies are summarized. Furthermore, some typical silicon spheres are shown in figures 1 to 5.

Simple silicon spheres occur very rarely (figure 1). Most frequently, metallic inclusions are surrounded with bubbles. There were found spheres surrounded by many small bubbles and spheres surrounded by a few big bubbles. The big bubbles are long-stretched and vertically arranged to the additionally observed cords (figures 2 and 3). Smaller spheres are formed very often at the surface of the silicon spheres.

By polarized light a strong refraction is observed around the spheres, which is due to stresses between glass and metallic inclusion. During the cooling process

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Table 1. Results of classification of silicon spheres observed in industrial flint glass samples

	sample series 1	sample series 2	sample series 3	sample series 4
simple silicon sphere	6.7%	2.0%	2.8%	2.8%
silicon sphere with bubbles	59.5%	55.3%	68.6%	58.3%
silicon sphere with stress cracks	33.8%	42.7%	28.6%	38.9%
sphere diameter in mm[1)]	0.87 ± 0.2	0.75 ± 0.2	0.62 ± 0.2	0.93 ± 0.2

[1)] Mean value with standard deviation.

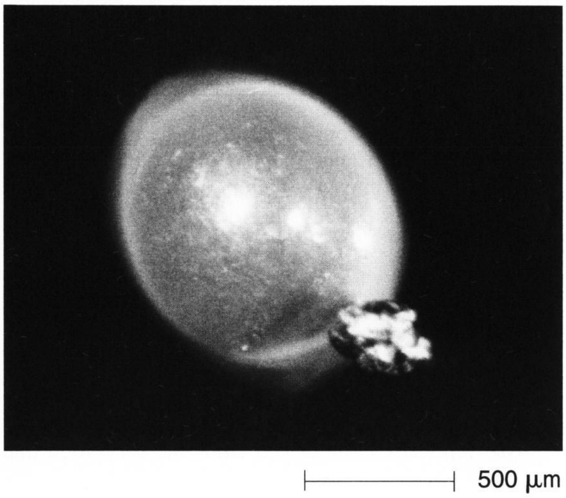


Figure 1. Simple silicon sphere with a smaller sphere at the surface (investigated under reflected-light microscope).

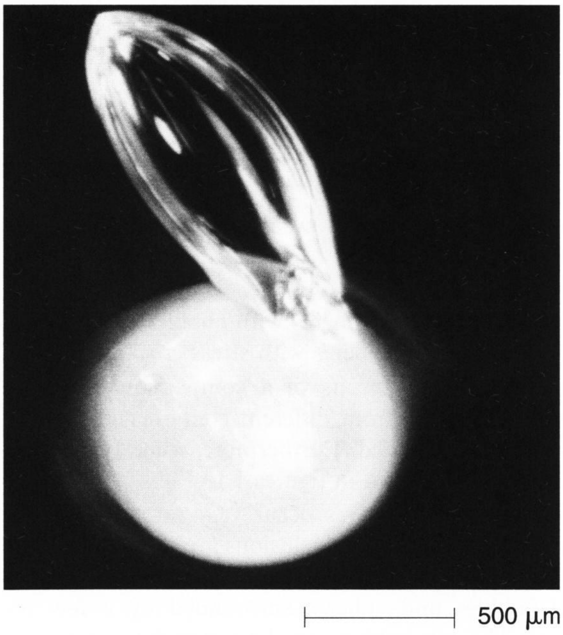


Figure 2. Silicon sphere with a long-stretched bubble (investigated under reflected-light microscope).

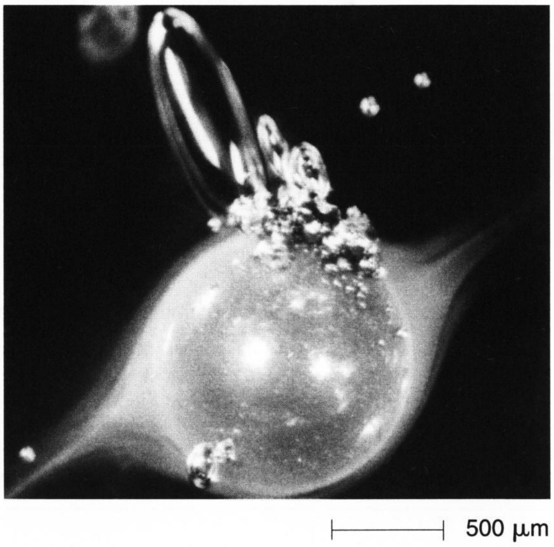


Figure 3. Silicon sphere with cords arranged radially and bubbles arranged vertically (investigated under reflected-light microscope).

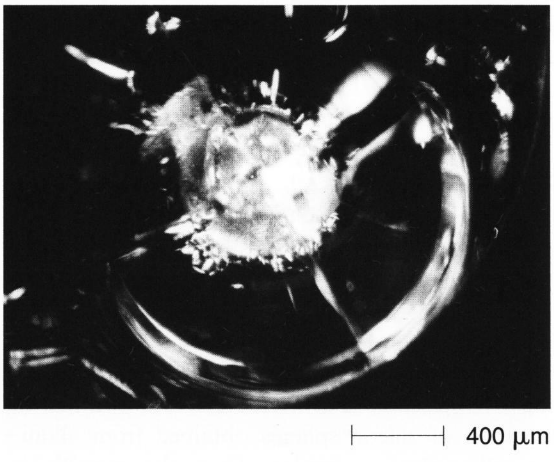


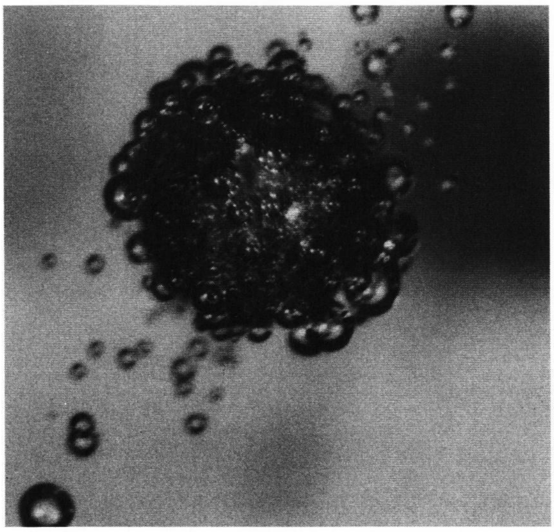
Figure 4. Silicon sphere with radial and elliptical stress cracks (investigated under reflected-light microscope).

these stresses are built up around the metallic inclusions due to different thermal expansion coefficients (α_{Si} = 2.5 · 10^{-6} K^{-1}, α_{glass} = 9 · 10^{-6} K^{-1}). In figure 4, radial and elliptical stress cracks formed around the silicon spheres are shown.

The cords observed were examined using the Schearing method at the Interphako Jenapol microscope. The refraction difference measured between glass and cord is negative. Thus, the cords consist of silicon oxide.

625 μm

Figure 5. Oval silicon sphere (investigated under reflected-light microscope).



500 μm

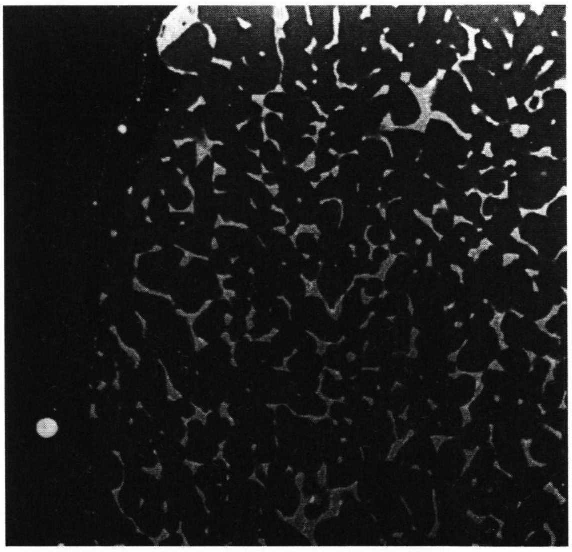
Figure 6. Silicon sphere with many small bubbles obtained in amber glass (investigated under reflected-light microscope).

The silicon spheres from production processes have a mean size of (0.80 ± 0.20) mm. This uniform sphere size is assigned to a long residence time of silicon spheres in the glass melt. However, the time was too short for complete dissolution of the metal. Figure 5 shows an oval silicon sphere. This shape is attributed to the liquid state of the metallic sphere in the melt. The silicon spheres did not dissolve at a higher melting temperature either.

In the case of green and amber glasses the silicon spheres formed were also examined, however, not so thoroughly. The silicon spheres have a mean size of (0.80 ± 0.37) mm. In figures 6 and 7 typical silicon

500 μm

Figure 7. Silicon sphere with radial stress cracks obtained in green glass (investigated under reflected-light microscope).



40 μm

Figure 8. BSE micrograph of a silicon sphere.

spheres are shown. The appearance of the metallic inclusions is also dominated by many very small bubbles, cords, stress cracks and smaller silicon spheres at the surface of the spheres.

The silicon spheres formed in the container glass melt are easily fissionable, but stick strongly to the surrounding glass.

2.2 Scanning electron microscopy

The glass samples containing silicon spheres were prepared for studies using the scanning electron microscope DSM 900/Zeiss, Oberkochen (Germany). With the aid of X-ray analyses, the composition of the silicon spheres was determined. The composition of silicon spheres in samples from different container glass companies is similar. As shown in figure 8, the silicon spheres in flint

Table 2. Composition (element concentration in wt%) of the dark phase contained in silicon spheres from flint glass determined with X-ray analysis

element	sample series 1	sample series 2	sample series 3	sample series 4
Si	96.2 ± 2.4[1)]	95.5 ± 1.9[1)]	96.4 ± 1.3[1)]	97.7 ± 0.7[1)]
O	0.6 to 6.5	0 to 5.2	–	–
Ti	0 to 0.3	–	0 to 0.4	–
Fe	0 to 2.5	–	–	–
Sn	0 to 0.6	–	–	–
Na	0 to 0.2	0 to 0.3	0.2 ± 0.04[1)]	0.3 ± 0.05[1)]
P	0 to 0.2	–	–	–
Zn	0 to 1.2	–	–	–
F	–	0 to 2.3	–	–
Cu	–	–	0 to 1.0	–
S	–	–	–	0 to 0.2

[1)] Mean value with standard deviation.

Table 3. Composition (element concentration in wt%) of the light phase contained in silicon spheres from flint glass determined with X-ray analysis

element	sample series 1	sample series 2	sample series 3	sample series 4
Si	49.8 ± 7.0[1)]	47.7 ± 5.6[1)]	41.3 ± 2.2[1)]	40.4 ± 4.0[1)]
O	0.2 to 2.3	–	–	0 to 1.2
Mg	–	–	–	–
Al	–	–	–	–
Ti	0.1 to 5.8	0 to 6.3	6.2 ± 4.2[1)]	5.7 ± 3.0[1)]
Mn	1.5 to 29.8	3.2 ± 1.2[1)]	1.4 ± 0.4[1)]	9.0 ± 4.2[1)]
Fe	35.0 ± 9.4[1)]	42.4 ± 3.3[1)]	4.2 ± 1.6[1)]	40.8 ± 2.9[1)]
Sn	0 to 0.5	–	–	–
Cr	0.3 to 0.6	0 to 1.5	2.2 ± 1.27[1)]	0.7 ± 0.07[1)]
P	0 to 0.4	0 to 0.5	0 to 0.5	0.4 ± 0.1[1)]
Cu	0 to 5.2	0 to 2.4	38.0 ± 4.2[1)]	0 to 5.5
Zn	0 to 2.2	0 to 2.4	4.0 ± 1.2[1)]	0 to 8.0
Pb	0 to 5.0	–	0 to 1.8	0 to 0.4
F	0 to 7.9	0 to 1.9	0 to 1.0	0 to 0.8
Na	0 to 0.3	0 to 0.4	0 to 0.3	0 to 0.3
S	0 to 0.5	–	–	0 to 0.1

[1)] Mean value with standard deviation.

glass consist of a dark matrix phase in which a lighter phase is embedded. The light phase in turn is composed of different phases. However, these phases could not be analyzed separately due to their small size (<5 μm).

The results of X-ray analyses of these phases are summarized in tables 2 and 3. The dark phase contains silicon and small concentrations of other elements. The main elements of the light phase are silicon and iron. Only in the samples from Vetropack Austria a high content of copper was found. The concentrations of manganese, copper, zinc, lead, fluorine and titanium in this phase fluctuate strongly, which is attributed to the different phases contained. Consequently for these elements the mean value with standard deviation could not be calculated. A high concentration of these elements as in the case of manganese (see table 3, sample series 1) is a runaway. Often the Si : Fe mole ratio was 1 : 2, accordingly a $FeSi_2$ phase has been formed.

Corresponding to studies by light microscopy, smaller silicon spheres were observed around the silicon spheres. Figures 9 and 10 show that the smaller spheres are sometimes connected with the initial sphere or they are already separated. These spheres contain a higher quantity of light phase as well as more different phases. Furthermore, the composition of the alloys differs from sphere to sphere.

Beside these spheres of 50 to 100 μm in diameter also many spheres smaller than 5 μm were formed. As shown in figures 8 and 9, these very small particles are arranged circularly around the silicon spheres in a distance of about 5 μm.

The amber and green glass samples examined also contain silicon spheres composed of a silicon-rich matrix phase and a phase appearing lighter. The main constituents of the light phase are silicon, iron and chromium. Otherwise, some samples contain manganese and copper as further main constituents in this phase. The quantity of the light phase in the matrix phase of silicon differs from sample to sample. This result confirms that the composition of this phase depends on the concentration

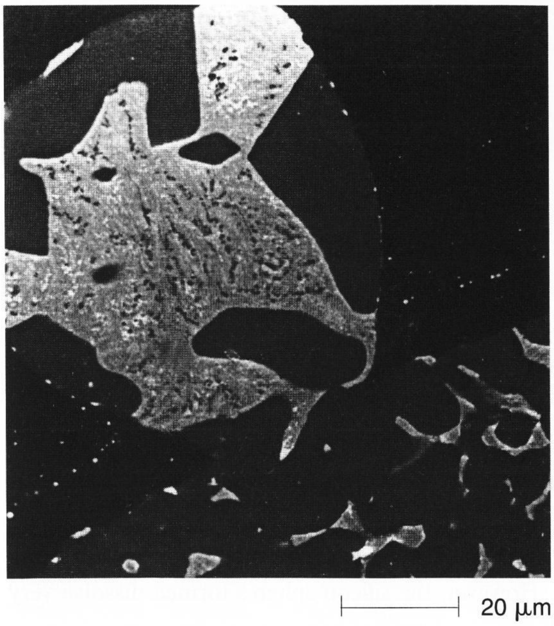


Figure 9. BSE micrograph of a smaller silicon sphere at the surface of the initial silicon sphere.

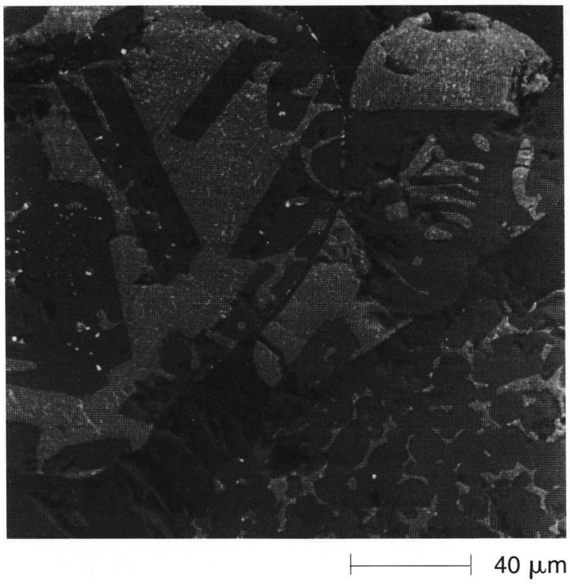


Figure 10. BSE micrograph of two smaller silicon spheres beside the initial silicon sphere.

of polyvalent ions in the melt and on the diffusion of the reduced elements to the metallic spheres. Furthermore, the melting time as well as the melting temperature influence the structure of the silicon spheres.

3. Silicon spheres produced in laboratory melts

3.1 Silicon spheres formed by aluminothermy

For the comparison with the results from the industrial samples, silicon spheres have been produced by aluminothermic reduction of silicon oxide. The reaction was carried out corresponding to the instruction in [6],

$$3SiO_2 + 4Al \rightarrow 2Al_2O_3 + 3Si \,. \qquad (1)$$

The silicon spheres obtained have a mean size of 1 cm. By means of X-ray diffraction method, it could be shown that the spheres are composed of two phases. These phases are a pure silicon phase and an aluminum–silicon phase with a composition of 0.87 mol Al and 0.13 mol Si. Using electron microscopy a further aluminum–silicon–iron phase was found. In table 4 the results of the EDX analyses are given. As shown in figure 11, the main phase is an aluminum–silicon alloy, in which a silicon phase (smooth phase) and an aluminum–silicon–iron phase (needle phase) are embedded. Such structures appear when aluminum can not dissolve and therefore, a local surplus of aluminum occurs. The composition of the aluminum–silicon phase fluctuates between the following compositions (in wt%):

a) 67.3 Al, 30.6 Si, 2.6 O and
b) 95.4 Al, 2.8 Si, 1.6 O.

The composition of the aluminum–silicon–iron phase is dominated by the compound Al_3FeSi_2.

The aluminothermically formed spheres are also stable in the container glass melt and only decompose when melting temperatures exceed 1200 °C for a long time.

3.2 Silicon spheres formed by adding metallic cuttings

The melting conditions of the laboratory melts with added aluminum and magnesium cuttings are already described in a previous publication [3]. Melts were carried out varying the amount of metal as well as melts varying the melting volume, the quantity of refining agent, the melting time and the melting temperature. The studies have shown that the formation of silicon is due to the introduction of the metal and can be described by the following reaction (2) in the container glass melt,

$$Na_2Ca_3Si_6O_{16} + 2Al + 1/2O_2 \rightarrow Al_2SiO_5 + \\ + Si + Na_2Ca_2Si_3O_9 + CaSiO_3 \,. \qquad (2)$$

At melting temperatures of 1100 and 1200 °C as well as at quantities of aluminum over 0.5 g/100 g glass and short melting times, strong gray-black colorations of the glass melt were observed. These colored glass regions also contain silicon, however, these particles are not comparable with the silicon spheres from industry due to their small size. In this paper the results of investigations of the silicon spheres prepared at melting temperatures of 1400 and 1500 °C are presented.

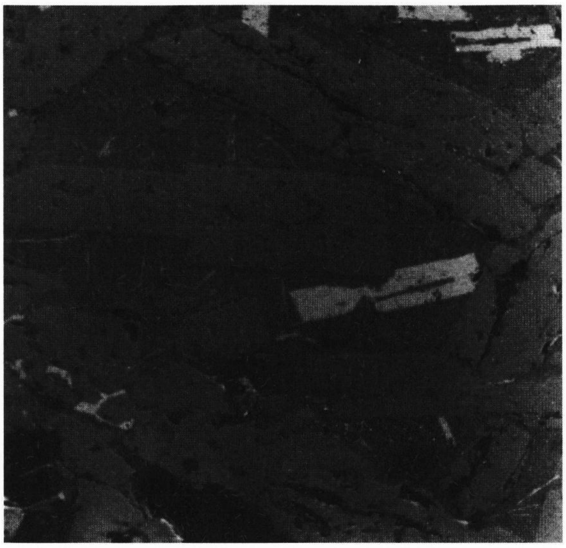


Figure 11. BSE micrograph of phases in a silicon sphere formed by aluminothermy.

3.2.1 Light microscopy

The silicon spheres obtained in laboratory melts are similar to the silicon spheres in samples from the industrial production. The spheres are also surrounded with many bubbles, stress cracks and cords. Furthermore, smaller spheres were also found at the surface. Bubbles especially were observed in amber glass melts and at long annealing times.

In contrast to flint glass samples from industry the silicon spheres from laboratory melts containing flint glass cullet are often surrounded with brown cords. Furthermore, a gray-colored glass region around the metallic inclusions was observed in amber glass melts.

3.2.2 Scanning electron microscopy

It was found by scanning electron microscopy that the silicon spheres obtained are either homogeneous or composed of two phases, which appear in the scanning electron micrograph as a dark and a light phase. The compositions of the dark and the light phase are similar to those of the samples of the production process.

The gray-colored glass region formed around the silicon spheres in amber glass melts was examined by line scan analyses. The main constituent of the gray-colored region is silicon. Copper and iron are also enriched at some positions.

4. Results and discussion

The studies of silicon spheres using light and electron microscopy confirm that independent of the introduced metal always silicon spheres with a similar structure are formed in alkali–lime–silica glass.

In contrast to the container glass samples from different companies, the glass melts prepared in laboratory are often gray-black colored. From this result it is concluded that the metals added dissolve better due to a higher glass volume and stronger currents in a melting tank. However, the silicon spheres formed dissolve very slowly.

Corresponding to Weiser et al. [2] and Wohlleben et al. [7] the metallic inclusions consist of a silicon-rich main phase in which a light phase is embedded. The light phase is composed of different phases. The main elements are silicon and iron. Further elements such as titanium, manganese, chromium, zinc, lead, copper in very small concentrations were found in flint glass. In amber and green glass chromium, manganese and copper are also enriched in these phases.

The compositions of obtained alloys depend on the concentration of polyvalent ions in the melt, melting temperature and melting time. If silicon spheres stay for a long time in the melt, then they always contain alloying phases.

The viscosity of the melt is decreased by high additions of aluminum. Thus, the reduced metallic elements can not diffuse into the silicon spheres and accordingly homogeneous silicon spheres are found in these flint glass melts. Metallic spheres containing an aluminum–silicon matrix phase can also be formed, when a local surplus of aluminum exists. This case is observed in a gray-black colored sample from the bottom of the crucible [3]. Weiser et al. [2] also found similar inclusions in some dip samples taken out of a melting tank.

Table 4. Composition of aluminothermically formed silicon spheres determined with EDX analysis

sample no.	composition (element in wt%)								
	rough main phase				smooth phase		light needle phase		
	O	Al	Si	Fe	O	Si	Al	Si	Fe
1	2.2	69.8	27.8	–	2.0	98.0	42.4	26.7	30.9
2	1.7	96.2	1.6	0.4	2.1	97.8	55.3	16.5	28.2
3	2.0	64.7	33.3	–	1.6	98.4	54.4	17.0	28.7
4	1.6	96.3	2.0	–	1.2	98.8	–	–	–
5	1.5	93.6	4.7	–	0.9	99.0	54.2	17.1	28.6
6	1.8	67.3	30.8	–	1.2	98.5	41.9	27.2	30.9

The silicon spheres obtained from industry are inclusions which have been for a long time in the container glass melt. However, from the spherical shape, it is concluded that the temperatures in the melt are in general higher than the melting temperature of the elementary silicon. During the annealing process the silicon spheres split off smaller spheres. The composition of these metallic spheres fluctuates strongly due to different forming conditions such as the size of the starting metallic sphere, the quantity and composition of alloys contained, and the temperature.

The deformation of the spherical shape, the appearance of smaller spheres and of bubbles indicate the dissolution process of the metallic inclusions. The dissolution behavior of silicon spheres was also investigated. The results will be reported in a further publication.

5. Conclusions

These investigations have shown that metallic silicon spheres occur in the container glass melt if metals such as aluminum enter the melting tank. The silicon spheres obtained have a similar structure in the alkali–lime–silica glass. The polyvalent ions in the melt are reduced. The reduced metallic elements diffuse into the silicon spheres and form further phases in the silicon-rich matrix phase.

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6. References

[1] Schumacher, L.: Entstehung von elementarem Silicium in einer Grünglasschmelze bei extrem hohem Scherbenzusatz. Presented at: Meeting of Technical Committee III of DGG on April 9, 1975 in Frankfurt/M.

[2] Weiser, S.; Leblanc, J.; Kilpatrick, B.: How aluminum metal contamination affects container production. Glass Ind. **67** (1986) no. 7, p. 18/23.

[3] Reisch, R.; Stachel, D.; Traufelder, S. et al.: Thermal behavior of aluminum in a container glass melt. Glastech. Ber. Glass Sci. Technol. **69** (1996) no. 5, p. 123–130.

[4] Jebsen-Marwedel, H.; Brückner, R. (eds.): Glastechnische Fabrikationsfehler. 3. Aufl. Berlin (et al.): Springer, 1980. p. 291–292.

[5] Führ, B.; Zippe, B.-H.; Drescher, H.: Neue Technologie beim Altglasrecycling: die Glasvermahlung. Glastech. Ber. Glass Sci. Technol. **68** (1995) no. 5, p. N63–N69.

[6] Jander, G.; Blasius, E.: Lehrbuch der analytischen und präparativen anorganischen Chemie. 10. Aufl. Leipzig: Hirzel, 1973.

[7] Wohlleben, K.; Woelk, H.; Konopicky, K.: Untersuchung kugeliger Einschlüsse im Flachglas mit Hilfe der Elektronenstrahlmikrosonde. Glastech. Ber. **39** (1966) no. 7, p. 329–332.

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Addresses of the authors:
R. Reisch
Ossmaritz Nr. 5, D-07751 Ossmaritz

D. Stachel, E. Tessmann
Friedrich-Schiller-Universität, Otto-Schott-Institut
Fraunhoferstraße 6, D-07743 Jena