# Is there a Problem with the Nickel Sulfide NiS in Toughened Borosilicate Glass?

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## 1. Introducing remarks

Nickel sulfide NiS causes spontaneous cracks in toughened flat glass even after years because of a delayed phase transition with increase of the volume. Therefore, the heat-soak-test must be provide for these products. The common flat/float glass is a soda-lime-silicate glass. Since it seems to be impossible to eliminate every source of nickel from the glass batch, the presence of nickelsulfidic inclusions is a proven fact. Until today, the interaction with the glass melt and nickel resp. nickel sulfides is not understood in all details. Some investigations were done to clear these processes, which can prevent the destroying of the toughened flat glass by the NiS during phase transformation [1,2,3,4]. During the last years, the borosilicate glass type get more interesting as an active construction element in the building sector, above all because of its improved properties related to normal soda-lime glass (much lower thermal expansion coefficients, higher strength and resistance against high temperatures for fire preventing and blocking systems).

The goal of this project was to clear what happens with nickel sulfides in borosilicate glass melts, which interactions between melt and nickel sulfides will occur, and whether a heat-soak-test is necessary or not.

Former investigations showed, that it is not possible to form nickel sulfide phases in borosilicate glass melts, even if strong conditions were applied [5,7]. But, what is to expect, *when* inserted nickel sulfides occur in the borosilicate glass?

## 2. Experimental procedures

For the planned investigations, two different compositions of nickel sulfides, $Ni_3S_2$ and NiS, where prepared in a sealed $SiO_2$ glass tube at temperatures of 750°C resp. 850°C in an electric oven. After quenching, the regulus was crashed and small spheres formed from the pieces in a KCl melt at 1150°C. The nickel sulfide spheres were imbedded into a special resin, their surface grinded and polished and after covering with carbon, characterized by Scanning Electron Microscopy (Zeiss DSM 940A) and microprobe analysis system (LINK exl 10). The EDX analyses were done at 20 kV with Be window, the calculation was made with gain calibration by a Cobalt standard and $FeS_2$ etalon after PHI-RHO-Z modus. Then the spheres were isolated from the resin, cleaned, weighted and finally inserted (1 sphere for each crucible) into two different types of borosilicate glass melts (Borofloat 33 and Borofloat 40) at different temperatures (1350°, 1450°, or 1550°C) and different times (30 or 60 minutes) of exposure in an electric heated furnace. There were used only original cullets for remelting, crucible material was $SiO_2$ . After experiment, the glass melts were rapidly cooled at air to freeze-in the obtained state of the nickel sulfidic phase(s). Documentation with optical microscopy, isolation of the nickel inclusions from the glass, weighting and a new preparation procedure for the investigation under the Scanning Electron Microscope and microprobe analyses followed (see above). The nickel sulfide spheres were only used for one melt experiment (1 cycle). The relation between nickel and sulphur was determined for each of the obtained microphases inside the spheres, if phase separation was found. Also, a representative area was measured to fit the relation between the phases.

## 3. Results of experiments

### 3.1 Chemical composition of the nickel sulfides before and after melt procedure

Nickel sulfides will undergo changes in chemical composition, when they have contact with air at high temperatures. They will oxidize spontaneously [8], where the nickel sulfides eliminate "$SO_2$" and form NiO, finally:

$$2\,Ni_3S_2 + 7\,O_2 \;=>\; 6\,NiO + 4\,SO_2 \;\Rightarrow\; \Delta G_R = -\,206\ \text{kJ mol}^{-1}\ \text{Ni}\ (1425°\text{C})$$

$$2\,NiS + 3\,O_2 \;=>\; 2\,NiO + 2\,SO_2 \;\Rightarrow\; \Delta G_R = -\,300\ \text{kJ mol}^{-1}\text{Ni}\ (1425°\text{C})$$

This also depends primary on the contact with oxygen through the surface of the spheres, by this reason, the oxydation process can be only partially. But, at these temperatures in the glass melts, the nickel sulfides are liquid. The substance contact and transport is not hindered kinetically, so the reactions occur in a short time. The result of oxidation process only depends on offer of "active" oxygen in the glass melt. Secondly, the equilibria between oxygen and sulphur species will determine the oxydation route. Under strongly reducing conditions, no (or nearly no) oxygen is available for the oxydation processes. So, very different interactions with the nickel sulfides and the melt will be obtained in these cases. The used borosilicate glass melts do not contain any sulphur species and the fining and melting is oxidizing, so a complete different behaviour of the nickel sulfides in the glass melt, related to normal soda-lime glass, is to expect.

When partial oxydation processes took place, the structures of the nickel sulfides become inhomogeniously [6], above all, the prepared NiS particles, first during sphere forming in the KCl melt and after much stronger, in the glass melt. Depending on real conditions, the relation between the found phases is different, for example:

| Sample | Temperature | Time | S: Ni before melting | S: Ni after melting | Difference |
|---|---|---|---|---|---|
| 12 | 1350°C | 30 min | $NiS_{0.82}$ | $NiS_{0.20}$ | 0.62 |
| 16 | 1450°C | 30 min | $NiS_{0.82}$ | $NiS_{0.12}$ | 0.70 |
| 15 | 1550°C | 60 min | $NiS_{0.80}$ | $NiS_{0.05}$ | 0.75 |

The starting composition was $NiS_{1.00}$ in all cases. The loss of sulphur during experimental procedure characterizes the intensity and completeness of the partial oxidation processes within the borosilicate glass melt. When using $Ni_3S_2$, we found:

| | | | | | |
|---|---|---|---|---|---|
| 33 | 1350°C | 30 min | $NiS_{0.65}$ | $NiS_{0.26}$ | 0.39 |
| 23 | 1450°C | 30 min | $NiS_{0.65}$ | $NiS_{0.16}$ | 0.49 |
| 21 | 1550°C | 60 min | $NiS_{0.65}$ | $NiS_{0.12}$ | 0.53 |

### 3.2. Microstructure of the nickel sulfide spheres before and after processing

The analysis of the chemical composition of the microphases is necessary to check the oxidation route. So it will be possible to formulate specific reaction equations by help of the compositions before and after. Before the processing, the $Ni_3S_2$ spheres mostly were homogeniously with exactly this composition. Only in some cases, the $Ni_7S_6$ phase was found as the minor component. These experiments were done only with single-phase $Ni_3S_2$ spheres.

Concerning NiS, already in the KCl melt at 1150°C, a change in structure and composition was obtained. We got spheres with mostly 2 phases: NiS and $Ni_3S_2$. This is caused by partial oxydation of the NiS phase, e.g.:

$$10\ NiS + O_2 \Rightarrow 7\ NiS + Ni_3S_2 + SO_2 \qquad \Delta G_R = -294\ kJ\ mol^{-1}\ Ni\ (1425°C)$$

This partial oxydation, also is thermodynamic preferred. The value of GIBBS free reaction enthalpy depends on relation between the formed phases and temperature. This way, it is not surprisingly, that at melt exposure conditions the nickel will oxidize into NiO, finally. The processes of the partial oxidation as well of the final forming of NiO turn out parallel. But, it is not possible with our analysing system to determine the value of NiO in the samples and the relation between elementary nickel and nickel oxide.

Resulting chemical reactions:

Sample 12: $95\ NiS + 7\ Ni_3S_2 + 93(+x)\ O_2 \Rightarrow 8\ Ni_3S_2 + 92\ (Ni+xNiO) + 93\ SO_2$

Sample 16: $95\ NiS + 7\ Ni_3S_2 + 93(+y)\ O_2 \Rightarrow 8\ Ni_3S_2 + 92\ (Ni+yNiO) + 93\ SO_2$

Sample 15: $83\ NiS + 7\ Ni_3S_2 + 93(+z)\ O_2 \Rightarrow 2\ Ni_3S_2 + 98\ (Ni+zNiO) + 93\ SO_2$

Sample 33: $43\ Ni_3S_2 + 58(+a)\ O_2 \Rightarrow 14\ Ni_3S_2 + 87\ (Ni+aNiO) + 58\ SO_2$

Sample 23: $37\ Ni_3S_2 + 62(+b)\ O_2 \Rightarrow 6\ Ni_3S_2 + 93\ (Ni+bNiO) + 62\ SO_2$

Sample 21: $40\ Ni_3S_2 + 72(+c)\ O_2 \Rightarrow 4\ Ni_3S_2 + 96\ (Ni+cNiO) + 72\ SO_2$

$(x < y < z; a < b < c))$

The found phases are the same, independend on starting composition (NiS resp. $Ni_3S_2$). In all cases, $Ni_3S_2$, elementary Ni, and NiO were identified, see examples above. By SEM investigations, it is clearly seen, that the relation between the resulting phases is different after different experimental conditions. At lower temperatures and longer times of exposure, the nickel sulfidic phase decreases, where the elementary nickel and the nickel oxide increase. The microstructure of the nickel sulfide spheres after the done experiments constists of some $Ni_3S_2$ as the matrix phase, relatively big crystals of Ni and a fine-grained distributed elementary nickel phase, as well as a dendritic crystallized NiO phase. This phase has a high melting point (around 1900°C) and occurs always in solid form, which leads to the fissure of the spheres. The formed smaller particles will dissolve more rapidly in the melt, so the process of the decomposition by oxidation will be enhanced. In some melts, mostly at 1550°C and times higher than 30 minutes, no residual of a the inserted sphere was found.

## 4. Conclusions

In borosilicate glasses, there is no problem with NiS, since:

* this phase will be transformed very rapidly into $Ni_3S_2$, which has no crack potential

* the oxidation of the nickel sulfides in this type of glass finally leads to NiO.

The temperature within the borosilicate glass melt is very high related to the soda-lime glasses. In flint soda-lime glasses (flat glass type), the process of transformation results in NiS, caused by the sulphur content of the melts and the low value of avialable active oxygen. This is impossible in the borosilicate systems, when they do not contain "sulphur". Additionally, the dissolution of the nickel sulfidic species is clearly thermodynamically preferred related to its formation.

**By these reasons, the heat-soak-test is not necessary for toughened borosilicate float glass.**

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