Spontaneous Glass Breakage Caused by Nickel Sulphide (a Review)

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Keywords:

1= spontaneous breakage 2=toughened glass 3=nickel sulfide 4=Heat Soak Process

Abstract

During the glass melting process, and during the tempering process, the high temperature modification (α-NiS) forms, stable above 390°C. It does not transform during the processes because of too high cooling speeds: it is "frozen".

The volume of the β-NiS is by about 4% higher than that of the α-NiS. The α to β transformation puts an internal spot-wise stress on the glass.

Pressure causes the initiation of small semicircular flaws around the inclusion. These are stable until a certain critical diameter has been reached, depending on the inclusion's environmental stress situation inside the glass.

At room temperature, the α to β transformation is slow. It takes months to years. A spontaneous break is happening when the inclusion's growth oversteps a critical limit.

An incubation period is typical for NiS breakage. The retardation may range from a few months to a couple of years. It is caused by the different thermal dilatation coefficients of glass and NiS

Heat soaking following European standard EN14179-1, prescribes the toughened glass to be heated up to (290 ± 10)°C, and this temperature to be kept constant during at least two hours. Following research done in the past, this theoretically reduces the breakage probability to below 10^{-6} , i.e. less than one break on 400 t of glass per year.

Six years of practical experience with the new HST showed that indeed the breakage rate is very low now. In contrast to the time before implementation of the new HST standard, no more breaks of tested glass were reported following the author's knowledge.

Nevertheless, the conditions of the HST may be enhanced. Following new research results from the Grenoble University (France), and test results published by Japanese colleagues [25], lowering the temperature by 30 degrees would make the HST more safe and at the same time allow to reduce the soaking time, see oral presentation of Oussama Yousfi on this conference.

Introduction

The nickel sulphide problem, i.e. the spontaneous cracking of thermally toughened safety glass sheets, the so called „tempered glass"[1 to 10], is known as a quality and reputation problem since the late fifties of last century, and was first reported by Ballantyne in 1961 [11]. Glass producers have tried to solve the problem by primary measures, but as they were not completely successful it still remains a very actual problem in view of the increasing number of all glass facades of many modern buildings.

Break departure points

The break departure point of a tempered glass sheet destroyed by NiS appears typically in the middle of a „butterfly" whose wings are formed by two outstanding pentagonal or hexagonal glass pieces (image 1). Microanalysis of the stones at their centre always finds the two main elements nickel and sulphur in addition to very small quantities of other metals such as iron or copper. Micro-diffraction identifies Millerite (NiS) as the main component. On the other hand, the emergence of a "butterfly" is not a prove for the presence of a NiS inclusion. Also other punctual charge leading to the failure of toughened glass shows the same aspect because of the high energy storage inside the glass.

The stones have mostly a spherical form, sometimes they are slightly elliptic. This shows that during the glass melting process they must have been molten and not wetted by the glass. Consequently, like oil in water, they form droplets swimming in the glass melt. On the other hand, the surface of the stones is rough, indicating that a crystallization have happened during the cooling of the glass : allotropic phase transition from a high to a low temperature modification.

Allotropic transformation, thermal dilatation, chemical composition

This allotropic transformation is the real reason for the breakage. NiS inclusions undergo a phase transition, not related to a change in chemical composition, but with a growth of the crystal.

Theoretically this volume increase is calculated from structure data to be about 4%. Practical values of 2.2% are reported by [13]. Also other nickel-sulphur-compounds are existing, but they are not related to spontaneous failures of glass (e.g. Ni_7S_6, Ni_3S_4 or Ni_3S_2; for further information refer to e.g. [18]).

The thermal dilatation coefficient of the nickel sulphides with composition Ni_1S_1 (i.e. Millerite), was measured in our laboratories and found to be $14*10^{-6}$ (average for 20 - 300°C) and $16*10^{-6}$ (for the high temperature modification at 350 - 500°C), respectively. These values are always higher than those of glass ($9*10^{-6}$ in the same temperature range). Additionally, the α-NiS is theoretically able to contain higher amounts of sulphur (NiS_x with $1 \leq x < 1.08$), and in practice it always contains traces of iron. These $Ni(Fe_z)S_x$ are differing in some of their properties (e.g. in the temperature of their allotropic transformation, and the α to β transformation rate). We have recently published an article [19] to show how NiS inclusions can form from nickel-bearing steel particles. From thermodynamic calculations and laboratory trials it comes out that a sulfur excess in the NiS inclusions is highly improbable, but that a slight under-stoichiometric composition, or two-phase composition [20], are forming, also found in real inclusions from breakage in HST and on buildings. In the following text, for better readability, „NiS" is meant to include all of these different really existing subspecies.

Statistical findings

Particle sizes of the NiS inclusions are found to vary between 0.05 mm and about 0.6 mm, the average being about 0.2 mm (figure 1). All inclusions having destroyed a glass sheet are situated in the inner zone of the tempered glass, independently of the glasses' thickness, between 25 and 75% in height (figure 2). Nevertheless, we have no reason to think that NiS stones can only exist in the inner zone of the glass. They should be dissipated homogeneously all over the glass bulk. Merker [13] describes trials with inclusions from a drawn glass line. All tested samples contained NiS stones in different height, but in his laboratory oven only the samples with inner laying stones broke between 10 and about 40 minutes. Approximately half the number of the samples remained unbroken in two hours' testing time.

In our laboratories we have studied 224 break departure points coming out of heat soak test ovens and from buildings. In 212 of them (96.4%) we found nickel sulphide to be the cause of the break. The others were two salt bubbles, three refractory inclusions and seven breaks from HS process where no default was detectable. The latter may be „real" spontaneous breaks without any apparent cause, or thermo-mechanical breaks, i.e. they broke in HS process because of asymmetric heating or too fast local cooling, at a point where the glass was already slightly damaged. We think that those breaks in HS process not caused by the presence of a NiS stone would not have lead to a break on building. Heating up and cooling down the glass in the HS process can induce strong bending stresses in the glass plates, and under these extreme conditions never occurring under normal conditions it may happen that a break begins at a relatively weak point of the glass, e.g., a bubble or an indifferent stone.

Image 1:

Left: So-called „butterfly" at the departure point of a break caused by NiS

Right: NiS inclusion found at a break departure point

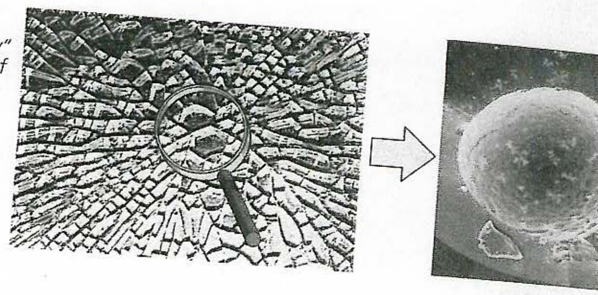


Figure 1:

Distribution of NiS stones' diameters found in broken glass. The average is about 200 µm.

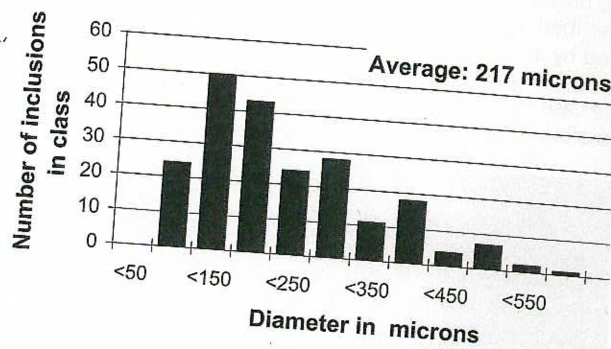
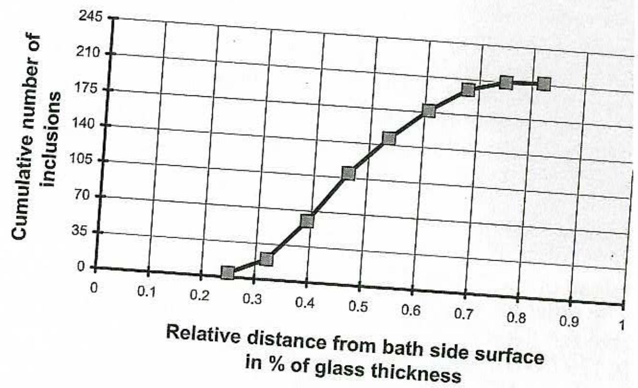


Figure 2:

Position of NiS stones having caused breakage.



Physical aspects

Apparently, NiS stones can only destroy tempered glass if they are situated in its tensile zone, and if they are large enough. This can be verified by physical modeling. The mechanical model relative to stresses around spherical inclusions with thermal expansion coefficients different from the matrix was first developed by Evans [15]. The model was further adapted by Hsiao to incorporate the NiS volumetric expansion [16]. Using this model, Swain showed that a critical diameter D_c exists, where the inclusion is able cause spontaneous fracture of glasses [16, 17]. The critical diameter depends on the residual stresses σ_0 around the inclusion (i.e. the level of tempering at the position of the stone inside the glass) :

$$D_c = \frac{\pi K_{1C}^2}{3{,}55\sqrt{P_0}\ \sigma_0^{1,5}} \quad \text{(EQ.1)}$$

with the stress intensity factor $K_{1C} = 0.76$ MPa*m$^{0.5}$ as a material constant for glass, and the hydrostatic pressure resulting from the α- to β-NiS transformation and from differences in thermal expansion coefficient $P_0 = 615$ MPa [16, 17]. Calculation shows that the theoretical minimum diameter (at maximum tensile stress) to destroy the glass is about 0.04 … 0.05 mm, in good agreement with the practical findings of, e.g., figure 1. The smallest inclusion we found up to date had a diameter of 60 µm.

NiS can only cause breakage when situated in the tensile zone of the glass. In the compressive zone, the stress initiated by NiS is (over)-compensated. Between the two extremes exists a transition zone where NiS stones are partly unable to break the glass.

Mechanism of spontaneous breakage caused by NiS stones

The following tempered glass destroying process („spontaneous failure") is generally acknowledged today:

During the glass melting process, in the furnace, the high temperature modification (α-NiS) is formed over intermediate steps of e.g. Ni_3S_2 [19],[21]. α-NiS is stable at temperatures higher than about 390°C. In glass sheets at room temperature, α-NiS is not (completely) transformed, because the cooling rate, at production, is too high for (complete) transformation. In addition, transformed NiS is exclusively able to destroy tempered glass sheets. This is why it is also not detectable by soaking annealed sheets.

By heating, during the tempering process, NiS is completely re-transformed into the α modification. The latter is mostly „frozen in" by blowing the sheet for tempering because the cooling rate is very fast.

At room temperature, the α to β transformation is slow. It takes months to years, and a spontaneous break is happening at the moment when the pressure on the glass around a NiS stone is high enough to initiate the destruction of the glass.

Because of the difference in thermal dilatation coefficients between glass and NiS stone, at room temperature, immediately after tempering, there is a hollow space (a spherical chink) around the inclusion, due to the differences in shrinking on cooling from T_g where glass becomes rigid. At T_g, the diameter of the cavity in the glass is fixed. Below this temperature, the NiS stone is more contracting than the surrounding glass. A chink is forming around the inclusion. This is the reason why the beginning of spontaneous breakage on buildings is usually postponed by one or two years: the first growth of the stones is absorbed by this empty space. Only after filling it completely, a NiS stone can cause pressure to the glass.

Pressure initiates one or several small semicircular flaws around the inclusion (image 2). These are stable, even in tempered glass, until a certain critical diameter of the flaw has been reached. The latter depends on the inclusion's environmental stress situation inside the glass. The higher the tensile stress, the smaller will be the critical radius of the initial crack (the stress at fracture is $\sigma_f = K_{Ic} / a^{1/2}$.).

The initial flaw can often be found inside the butterfly, on the „mirror" around the NiS stone.

Crack growth in the glass bulk depends only on the pressure and is not subject to static fatigue, only occurring in the presence of water. Static fatigue is described as the growth of cracks caused by a stress enhanced chemical reaction between water and glass [22]. In the case of NiS induced cracks, this is impossible.

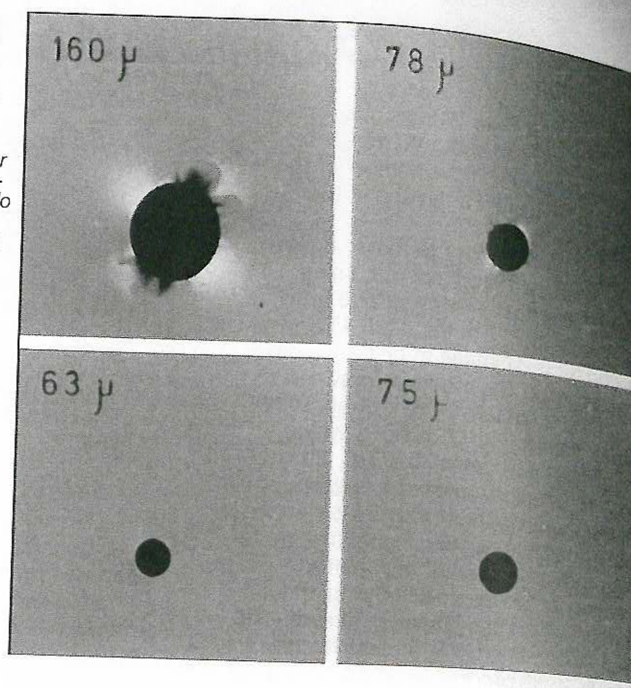
Heat Soaking

Already in the seventies, the Heat Soak (HS) process was developed to eliminate contaminated glass sheets. By this test, every glass sheet containing a critical NiS stone should be destroyed. After numerous tests, it was agreed that the test should consist in heating up to a certain temperature of e.g. 290°C, holding this temperature for a certain time, and cooling down to room temperature again (e.g. German DIN 18516). The procedure seems to be simple, but looking at the details it may become very complicated at the moment when the demand is to heat up the glass to a certain temperature instead of the furnace's air only.

In order to overcome the differences between the different countries, CEN-TC129 / WG2 has developed a new standard: EN14179-1, called "Heat Soak Tested Thermally Toughened Safety Glass", defining in this way a new product. It became fully effective in 2006, but the pre-standard was already adopted (and largely applied) in 2002. The most important task of this standard is to implement heat soaking conditions which guarantee a safe product, including a very low level of residual break rate. In very short, today's prescriptions are: to heat up the glass with a limited heating rate, then to keep it at (290 ± 10)°C during at least two hours, and to certify the HST furnace in order to make it operational with maximum performance. Practical tests have shown that in this way, the break rate of the un-soaked glass is reduced by more than 98.5% [23, 24]. Another practical observation is that since the introduction of the prEN 14179-1, no more claims have come up from any building equipped with heat soak tested glass.

In spite of those very convincing results, in the last years, doubts have come up about the question whether or not the temperature regime of the HST following EN14179-1 is really the best possible. Research at the Grenoble University (SIMAP) and certain laboratory tests carried out by our Japanese colleagues [25] show that the temperature should be ca. 30 degrees lower. More about this subject is referred by Oussama Yousfi in his speech and article at the actual GPD2009 [26].

Image 2: Flaws around NiS inclusions in annealed glass, final state after heat treatment, by polarized light microscopy. Depending on the size of the inclusions, smaller or bigger flaws are appearing. Smaller inclusions do not cause flaws; consequently their pressure is not sufficient to initiate the breakage of toughened glass.



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