

Nickel sulphide: new results to optimise the heat soak test for thermally toughened building glasses¹⁾

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The spontaneous failure of tempered façade glazings has been known as a security and reputation problem of these beautiful parts of the surface of modern buildings since the late fifties. By kinetic investigations on synthetic nickel sulphides and by statistical analysis of the breakage of heat soak test ovens it is shown that this problem can be solved. If the test is done in a right and careful way, at temperatures of $(290 \pm 10)^\circ\text{C}$, holding time need not be longer than 2 to 3 h to fulfil the implicit requirements of the German Standard (DIN 18516). On the other hand, literature data show that it should be possible to further shorten this holding time if it were possible to heat up faster and more homogeneously the glass to be tested.

Nickelsulfid: Neue Ergebnisse zur Optimierung des Heißlagerungstests für thermisch vorgespanntes Bauglas

Das durch Nickelsulfideinschlüsse verursachte Spontanbruchproblem vorgespannter Fassadenscheiben ist ein seit den späten fünfziger Jahren bekanntes Phänomen, das Sicherheit und Reputation dieser optisch ansprechenden Fassadenbestandteile bedroht. Durch kinetische Untersuchungen an synthetisch hergestellten Nickelsulfiden und durch Auswertung der Bruchstatistik in Heißlagerungstestöfen wird gezeigt, daß das Problem durch sorgfältige Durchführung dieses Tests gelöst werden kann. Bei richtiger Durchführung benötigt man nicht mehr als 2 bis 3 h Haltezeit bei $(290 \pm 10)^\circ\text{C}$, um die impliziten Anforderungen der Norm DIN 18516 zu erfüllen. Die Auswertung der spärlichen Literaturdaten zeigt aber, daß diese Zeit prinzipiell noch verkürzt werden könnte, wenn man das zu testende Glas schneller und gleichmäßiger auf die Testtemperatur aufheizen könnte.

1. Introduction

The nickel sulphide problem, i.e. the spontaneous cracking of thermally toughened safety glass sheets, the so-called "tempered glass" [1 to 10], has been known as a quality and reputation problem since the late fifties, and was first reported by Ballantyne [11]. Glass producers have tried to solve the problem by primary measures, but as they were not completely successful³⁾ it still remains a very current problem in view of the increasing number of all-glass façades of many modern buildings. The overall spontaneous breakage probability of glass was considerably decreased by technical measures, but it could not be reduced to zero. This is why e.g. still today, in Germany the complete number of glass sheets bearing a

security risk have to be tested by the so-called "Heat Soak Test" (HST), published in DIN 18516 [12], prescribing a constant test temperature of $(290 \pm 10)^\circ\text{C}$ during 8 h, but without stating whether this temperature is meant to be the glass temperature or the air temperature. In a great number of other countries, a similar test is also used, but often modified in duration (from less than 1 to more than 10 h) and in temperature (from 250 to 300°C, sometimes proposals even go up to 360°C during only a few minutes of holding time). Nevertheless, or just because of this, the problem remains topical because tempered glass on buildings is still failing spontaneously, and these failures are actually causing a severe reputation problem for tempered glass. Although only on a minor number of buildings breakage really occurs, this is almost sensationally reported in the press [e.g. 2 to 6] and subject to authority demands and political pressure [8]. The image of tempered glass as a façade material is considerably damaged and its use may be restricted by local or even national construction authorities.

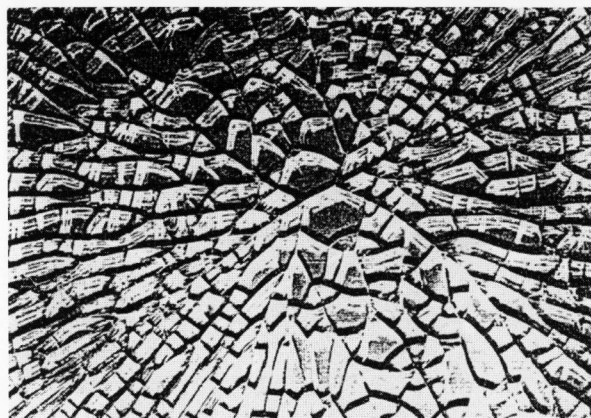
The starting point of break in a tempered glass sheet destroyed by NiS appears typically in the middle of a "butterfly", whose wings are formed by two outstanding penta- or hexagonal glass pieces (figure 1a). Micro-

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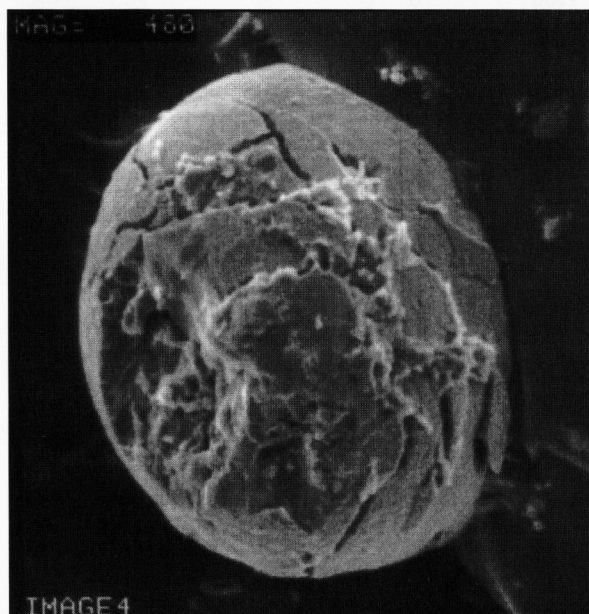
¹⁾ Presented in German at the 72nd Annual Meeting of the German Society of Glass Technology (DGG) in Münster (Germany) on 27 May 1998.

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³⁾ To make the reader aware of the work that would be necessary to solve the problem, it should be mentioned that just 1 g of nickel can make up to 70 000 NiS stones of 200 µm diameter. These may break the entire ten day's production of a float glass line (i.e. 5600 t of 8 mm thick glass in 4 m² sheets).



a)



b)

Figures 1a and b. The “butterfly”: characteristic break departure (figure a) and its cause: an NiS stone with a diameter of about 200 μm (figure b). The butterfly’s wings usually have a diameter of about 1 to 2 cm.

analysis of the stones always finds the two main elements nickel and sulphur in addition to very small quantities of other metals such as iron or copper. Microdiffraction identifies millerite as the main component, which is a naturally existing mineral with the chemical composition of Ni_1S_1 . The stones mostly have a spherical form (figure 1b), sometimes they are slightly elliptic. This shows that during the glass melting process they must have been molten⁴⁾ 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 crystallisation must have occurred during the cooling of the glass, i.e. allotropic phase transition from a high to a low temperature modification.

⁴⁾ Melting points of nickel sulphides: NiS: 976 °C; Ni_3S_2 : 787 °C; Ni_3S_4 : 995 °C; NiS_2 : 1022 °C [13].

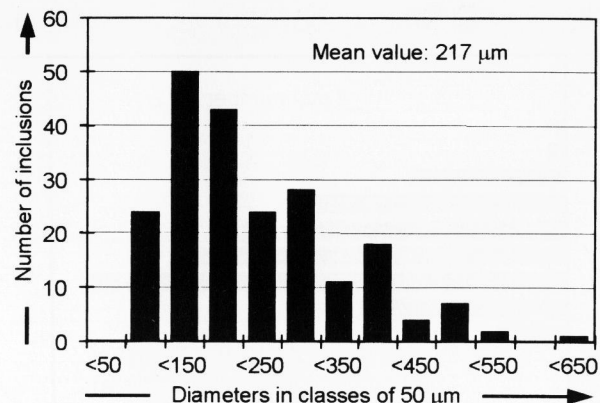
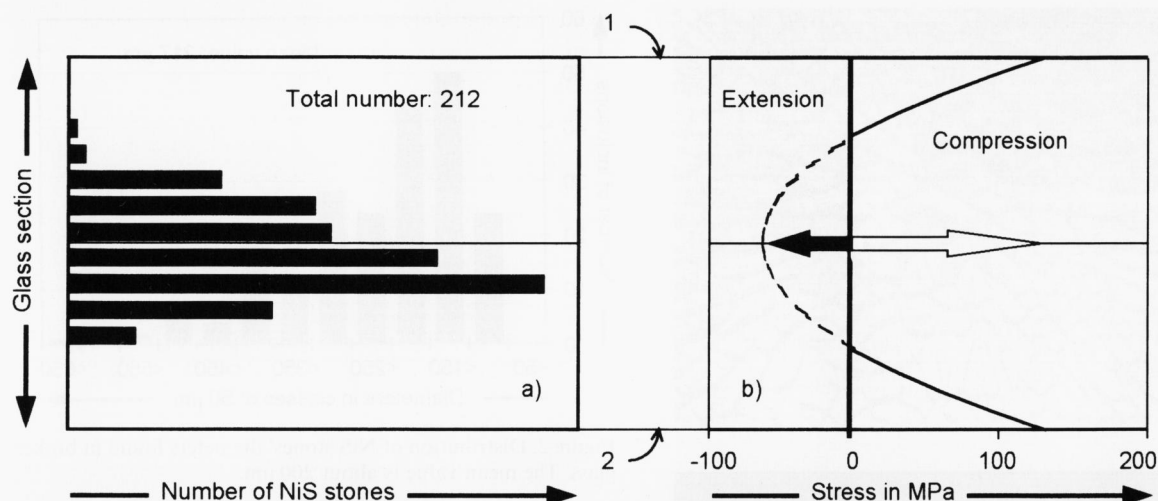


Figure 2. Distribution of NiS stones' diameters found in broken glass. The mean value is about 200 μm .

Particle sizes of the NiS inclusions are found to vary between 0.05 and about 0.6 mm, the average being about 0.2 mm (figure 2). All inclusions having destroyed a glass sheet are situated in the inner zone (between 25 and 75%) of the tempered glass, independently of the thickness of the glasses (figures 3a and b). Nevertheless, we have no reason to think that NiS stones can only exist in the inner zone of the glass. They should be distributed homogeneously all over the glass bulk. Merker [14] describes trials with inclusions from a drawn glass line. All tested samples contained NiS stones in different heights, but in his laboratory oven only the samples with stones in the inner zone broke between 10 and about 40 min. Approximately half the number of the samples remained unbroken in a testing time of 2 h.

In our laboratories we have studied 224 starting points of break in HST ovens and on buildings. In 212 of them (96.4%) we found nickel sulphide to be the cause of the break. The other failures were due to two salt bubbles, three refractory inclusions, and seven were from HST where no fault was detectable. The latter may be “really” spontaneous breaks without any apparent cause, or thermomechanical breaks, i.e. they broke in HST 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 HST not caused by presence of an NiS stone would not have led to a break on a building. Heating up and cooling down the glass in the HST 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 insignificant stone.

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 modelling. 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 [16] to incorporate the NiS volumetric expansion. Using this model, Swain [17 and 18] showed that there exists a criti-



Figures 3a and b. NiS stones having caused breaks; a) position of the inclusions in tempered glass in HST and on buildings; b) comparison with the residual stress curve in tempered glass. NiS only causes breaks when situated in the tensile zone. 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. 1: upper (atmosphere) side of the glass, 2: lower (tin bath) side.

cal diameter D_c of the inclusion to cause spontaneous fracture of glasses. 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):

$$D_c = \frac{\pi K_{IC}^2}{3.55 \sqrt{P_0} \sigma_0^{1.5}} \quad (1)$$

with the stress intensity factor $K_{IC} = 0.76 \text{ MPa} \cdot \text{m}^{1/2}$ 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 $P_0 = 615 \text{ MPa}$ [17 and 18]. Calculation shows that the theoretical minimum diameter (at maximum tensile stress) to destroy the glass is about 0.04 mm, in good agreement with the practical findings (figure 2). The smallest inclusion we found had a diameter of 54 μm .

So the destruction mechanism of tempered glass by NiS is principally well known. A certain number of nickel-sulphur compounds (e.g. Ni_7S_6 and NiS, but not Ni_3S_4 or Ni_3S_2 ; for the existing stoichiometric phases of Ni_yS_x refer to e.g. [19]) are subject to an allotropic phase transition related to a growth of the crystal by cooling, theoretically calculated from structure data to be about 4% for NiS.

The thermal dilatation coefficient of the nickel sulphides with composition Ni_1S_1 was measured in our laboratories and found to have a value of $14 \cdot 10^{-6}$ (on average for 20 to 300 °C) and $16 \cdot 10^{-6}$ (for the high-temperature modification at 350 to 500 °C), respectively. These values are always higher than those of glass ($9 \cdot 10^{-6}$ in the same temperature range). Additionally, α NiS can theoretically contain higher amounts of sul-

phur⁵⁾ (NiS_x with $1 \leq x < 1.08$) and in practice always contains traces of iron. These $\text{Ni}(\text{Fe}_2)\text{S}_x$ differ in some of their properties (e.g. in the temperature of their allotropic transformation, and the α to β transformation speed). In the following text, for better readability, "NiS" includes all of these different really existing subspecies.

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

a) During the glass melting process in the furnace, the high-temperature modification (α NiS) is formed, probably over intermediate steps of e.g. Ni_3S_2 [20 to 22]. This modification is stable at temperatures higher than about 390 °C. In the glass sheets, α NiS is not (completely) transformed, because the cooling speed is too high in the annealing process for (complete) transformation. In addition, transformed NiS cannot destroy untempered glass sheets. This is why it is also not detectable in sheets stored even over years in the warehouse.

b) By heating, during the tempering process, NiS is completely re-transformed into the α modification. The latter is mostly (to over 95%) "frozen-in" due to the fast cooling by air quenching in the tempering process.

⁵⁾ In terms of crystallography, this is a "lack-of-nickel" structure where a certain number of nickel places in the lattice are empty. The nomenclature NiS_x (with $x \geq 1$) is therefore not properly correct in the crystallographic sense, but for chemical composition (proportion of sulphur to nickel) it is right. We continue to use this nomenclature here to avoid confusion because we did so in our previous communications.

c) 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 pressure⁶⁾ in the glass around an NiS stone is high enough to initiate the destruction of the glass.

d) Because of the difference in thermal dilatation coefficients between the glass and the NiS stone, at room temperature, there is a hollow space⁷⁾ around the inclusion, due to the cooling from T_g where glass becomes rigid. At T_g , the diameter of the cavity in the glass is fixed, and the NiS stone is more contracting than the surrounding glass. This is the reason why the beginning of spontaneous breakage on buildings is normally postponed by one or two years: the first growth of the stones is absorbed by this empty space. Only after filling it completely the stones can cause pressure to the glass.

e) 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. The higher the tensile stress, the smaller will be the critical radius of the initial crack⁸⁾. The initial flaw can be traced back on the butterfly forming a "mirror" around the NiS stone. Crack growth depends only on the pressure and is not subject to static fatigue, which only occurs 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 [23]. In the case of NiS-induced cracks, this is impossible.

Already in the seventies, the HST was developed to find contaminated glass sheets. In this test, every glass sheet containing a dangerous NiS stone should be destroyed. It consists of heating up to a certain temperature of e.g. 290 °C, holding this temperature for a certain time (e.g. 8 h) and cooling down to room temperature again. 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 air.

The HST is expensive not only because of the investment and the running costs of the test oven, the manual and logistic work directly correlated to the working of the test, but also because of the necessity of reproducing and testing again the destroyed sheets. In many cases, the "exploding" sheet scratches its neighbours in a way that not only one but three sheets have to be reproduced. Delivery terms may be delayed.

It was reported that also heat-soaked glass sheets can break spontaneously in a very small number of cases. If we assume that these glass volumes have really been tested, we may think that the breaks happen because the

applications of the test differ in European countries in duration and temperature, but we don't find a correlation between e.g. the duration and these breaks. As already mentioned, the only standard exists in Germany [12]. In view of upgrading this German to a European Standard, in 1994, Saint-Gobain decided to treat the problem again in its laboratories. We hoped that the development of apparatus, methods and computers during the last 20 years might allow us to solve the related analytical and mathematical problems that seemed to be insoluble before. On the basis of a great number of existing publications three questions are raised:

First: Which NiS compositions are really dangerous for glass?

Second: How does the kinetics of the allotropic transformations of these dangerous stones influence the breakage risk?

Third: Which are the really optimised parameters for a good and reliable HST?

2. Experimental

2.1 Laboratory procedures and results

2.1.1 Synthesis of nickel sulphides

The first step to answer those questions was to produce synthetic Ni_yS_x species from pure nickel and sublimated sulphur powders [24]. In a second step, we also synthesised $Ni_y(Fe_z)S_x$ species having compositions of those which were analysed in real inclusions.

The synthetic nickel sulphides were kept in a refrigerator under protecting atmosphere because even at room temperature, their kinetic properties perceptibly change under air contact after a few weeks. It is also very important to carry out the kinetic trials under strictly inert atmosphere to avoid any contact with oxygen. Nickel sulphides are very sensitive to oxidation.

2.1.2 Characterisation of nickel sulphides

The inclusions found at spontaneous starting points of break were always and exclusively β NiS. The crystallographic analysis was done by a Siemens HiStar-Microdiffractometer, at the German Fraunhofer-Institut für Festkörper- und Werkstoff-Forschung in Dresden. Contrary to α NiS, β NiS is not able to form sulphur-richer forms, but has always the stoichiometric 1:1 composition, as was shown by high-resolution diffractometry.

Also in Dresden, the Ni_yS_x powders were characterised by a high-resolution STOE powder diffractometer. By comparison with literature [19, 25 and 26] we identified them to be Ni_3S_2 ; α Ni_7S_6 ; α Ni_1S_1 ; α $Ni_1S_{1.01}$; α $Ni_1S_{1.025}$; α $Ni_1S_{1.046}$; α $Ni_1S_{1.07}$.

With a new scanning electron microscope (SEM) with energy dispersive X-ray analyser (EDAX), we were able to exactly analyse the sulphur and iron contents of

⁶⁾ This is a tensile stress for the glass as well as a compressive stress. Only the tensile stress vector is responsible for destroying the glass sheets.

⁷⁾ In our opinion, the NiS stones don't stick to the surface of the cavity, but rather are located within the latter due to their rough surface (figure 1).

⁸⁾ The stress at fracture is $\sigma_f = K_{IC}/a^{1/2}$.

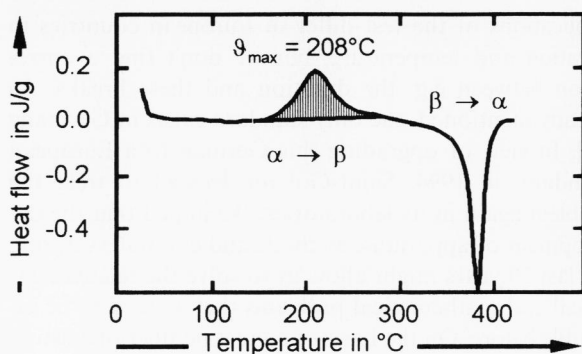


Figure 4. DSC curve of NiS_x for evaluation following the Kissinger method, e.g. at 30 K/min. The dependence of the maximum temperature of the exothermal peak on heating speed is evaluated.

the real inclusions on polished samples. For the composition $\text{Ni}_y(\text{Fe}_z)\text{S}_x$, we found $x = 1.000 \pm 0.005$, $y = 0.990 \pm 0.005$, and $z = 0.010 \pm 0.003$.

As already mentioned above, we synthesised five more synthetic powders in the range of these values: $\text{Ni}_{1.00}(\text{Fe}_{0.00})\text{S}_{1.00}$; $\text{Ni}_{0.99}(\text{Fe}_{0.01})\text{S}_{1.00}$; $\text{Ni}_{0.99}(\text{Fe}_{0.01})\text{S}_{1.01}$; $\text{Ni}_{0.98}(\text{Fe}_{0.02})\text{S}_{1.00}$; $\text{Ni}_{0.98}(\text{Fe}_{0.02})\text{S}_{1.01}$. These $\text{Ni}_y(\text{Fe}_z)\text{S}_x$ powders were characterised in our own laboratory because in the meantime we had acquired a sufficiently well-resolving X-ray diffraction apparatus. Chemical composition was examined by X-ray fluorescence and SEM/EDAX. We found the homogeneity of these powders to be good and the chemical composition to agree to what we had intended to synthesise.

In the transformed NiS_x powders which were obtained after the kinetic measurements by X-ray diffraction, besides the β NiS we sometimes found small portions of polydymite (Ni_3S_4). This must have been a transformation product of sulphur-rich NiS_x . So we think that probably the necessity of forming increasing amounts of this completely different species of a nickel sulphide from sulphur-rich NiS_x is the reason for the deceleration of the transformation speed (see below, and [14, 19 and 26] with increasing sulphur content of the starting composition. On the other hand, we never observed such high sulphur contents in the inclusions found in glass.

2.1.3 Kinetic measurements

Two different methods complementing each other were used for the kinetic measurements; they also overlap in a wide range in relation to our problem.

The first, differential scanning calorimetry (DSC) under helium with evaluation following the Kissinger method [27] can record kinetics of relatively fast transforming materials. From the relation between the transformation temperature and the heating speed, the parameters of the kinetic equation are calculated to describe the phase transition. An example of such a measurement is given in figure 4. Because we are interested

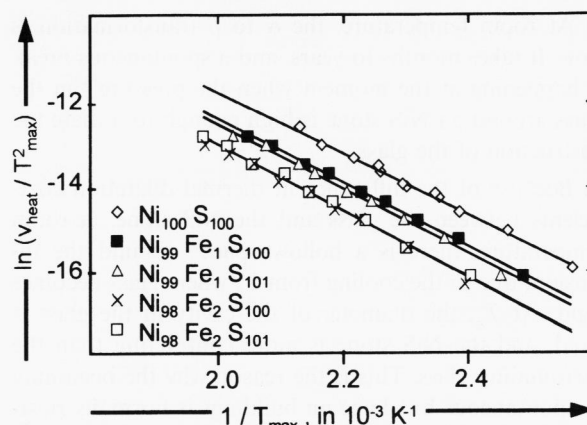


Figure 5. Kissinger graphs for different Ni(Fe)S species. Heating speed v_{heat} in K/s, T in K. Correlation coefficients of all linear fit lines are very good (0.998 in every case), indicating the validity of first order kinetic laws.

in the α to β transformation, the maximum of the first (exothermic) peak (T_{max}) is evaluated. Trials are repeated with different heating speeds (v_{heat}) and compositions, taking a fresh sample of about 100 mg for every assay. Kissinger graphs (figure 5) are calculated by plotting $\ln(v_{\text{heat}}/T_{\text{max}}^2)$ against the inverse of the absolute temperature.

From these, the parameters of the kinetic equations are calculated. In all cases, as expected, we found for a first order kinetic law

$$c(t) = c_0 \cdot e^{-kt} \quad (2)$$

with $c(t)$ = concentration of the remaining α phase at time t , c_0 = concentration at $t = 0$, k = the kinetic constant, and the temperature dependence of the kinetic constant given by

$$k(T) = Z_0 \cdot e^{-E_a/(RT)} \quad (3)$$

where $k(T)$ = the kinetic “constant” depending on the absolute temperature T , Z_0 = frequency factor, E_a = activation energy of the allotropic transformation, and R = the ideal gas constant was calculated following the Kissinger method for the phase transformations of every Ni_yS_x species, with exception to $\text{NiS}_{1.07}$ because of its unmeasurably slow phase transition, and Ni_3S_2 , not being subject to any allotropic transformation in the temperature range we investigated; we used the latter as an inert sample.

The second, a heating diffractometer, also under helium⁹⁾, allowed us to observe directly the increasing and decreasing of the characteristic diffraction peaks of the

⁹⁾ We also carried out some trials under air atmosphere. Kinetics decelerated very much and the results significantly differed from those under inert atmosphere. Because in glass inclusions at temperatures below T_g the atmosphere is strictly inert, results with possible oxygen contact of the samples cannot be applied to the behaviour of NiS stones.

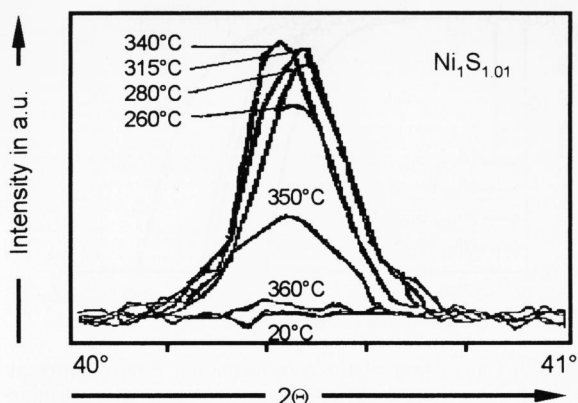


Figure 6. Appearance and disappearance of an X-ray diffraction peak of β NiS in dependence on the temperature. Primary radiation: Cu K α ; hkl: 211. The peak area is evaluated. (a.u.: arbitrary units.)

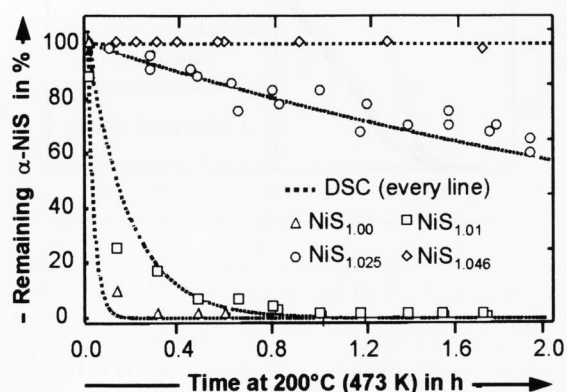


Figure 7. Comparison of the results of the Kissinger method (DSC: lines) with those obtained by the X-ray diffraction method (symbols) for different stoichiometries of NiS $_x$ at e.g. 200°C. The correlation between the two methods is very good except for fast kinetics where the X-ray diffraction method is too lazy.

α and β phases, respectively (figure 6). This method is useful for relatively slow transformation speeds. The peak areas of several peaks were used simultaneously, and we found a very good agreement between the results of the two methods (figure 7). Only for the high transformation speeds of NiS $_{1.00}$ and NiS $_{1.01}$, apparently, the diffraction method is too lazy. In these cases, only the results of the Kissinger method are reliable.

As the transformation speeds of the Ni $_y$ (Fe $_z$)S $_x$ were also rather fast, we only used the Kissinger method to measure their kinetics.

The summary of our results obtained in the last three years is represented in table 1 and partly in figure 8. It is seen that the results of our two syntheses and measuring series are slightly different. With respect to the time difference, the learning process about synthesis and handling of NiS and the fact that these results were ob-

Table 1. Kinetic data of nickel sulphides measured in Saint-Gobain laboratories: activation energies, E_a , and frequency factors, K_0 , found for different Ni $_y$ Fe $_z$ S $_x$ species

	E_a in kJ	K_0 in 1/s
Ni $_7$ S $_6$	329	$2.56 \cdot 10^{37}$
NiS (1997)	60	$4.62 \cdot 10^4$
NiS $_{1.01}$	63	$2.52 \cdot 10^4$
NiS $_{1.025}$	91	$2.26 \cdot 10^5$
NiS $_{1.046}$	486	$2.66 \cdot 10^{43}$
NiS $_{1.07}$?	?
NiS (1999)	60.6	$1.27 \cdot 10^5$
Ni $_{0.99}$ Fe $_{0.01}$ S	63.2	$1.33 \cdot 10^5$
Ni $_{0.99}$ Fe $_{0.01}$ S $_{1.01}$	63.8	$1.34 \cdot 10^5$
Ni $_{0.98}$ Fe $_{0.02}$ S	65.8	$1.38 \cdot 10^5$
Ni $_{0.98}$ Fe $_{0.02}$ S $_{1.01}$	65.7	$1.38 \cdot 10^5$

Note: Years in brackets indicate the time of the synthesis of chemically identical species. Slightly different results were found.

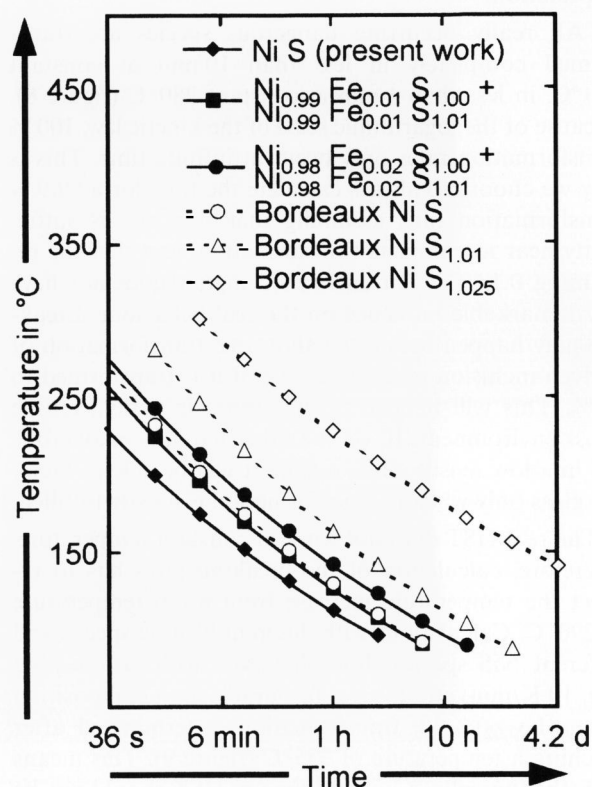


Figure 8. Time (in logarithmic scale) for complete (99.9%) transformation from α to β phase for different compositions of NiS $_x$ and Ni(Fe)S $_x$. Summary of the results of practically relevant kinetic measurements of different nickel sulphides. As far as we know today, NiS $_{1.025}$ and other species with higher sulphur content do not exist in float glass as inclusions. Every other species is transformed within 10 min at 250°C.

tained in two different laboratories¹⁰), with different apparatus and done by different people, we feel them to be in sufficient agreement.

¹⁰) The first set of trials on Ni $_y$ S $_x$ was carried out in the laboratory at Aubervilliers (France), the second set on Ni $_y$ (Fe $_z$)S $_x$ at Herzogenrath (Germany).

2.2 Interpretation of the laboratory results

a) During the HST, temperature must never be higher than 320°C. Above this temperature, back-transformation into α NiS might take place.

b) The transformation speed of Ni_7S_6 is so high that it is already transformed completely during tempering. So if there were inclusions of Ni_7S_6 in the glass, they would break it already in the tempering furnace. In accordance to this, to the authors' knowledge, this compound was never found as a main component in real NiS inclusions.

c) Principally, only NiS_x phases with x values between 1.00 and about 1.03 can be dangerous to tempered glass. At room temperature, only these are transformed fast enough to be able to break the glass in less than 100 years. As we never found sulphur contents higher than $x = 1.005$, from today's point of view, and considering a possible uncertainty of our analyses, we must exclude all compositions with $x > 1.01$ from our kinetic interpretation.

d) All really occurring dangerous species are transformed completely in less than 10 min at constant 250°C, in less than 1 min at constant 280°C (figure 8). Because of the logarithmic scale of the kinetic law, 100% transformation rates only occur at infinite time. This is why we choose to always calculate the time for a 99.9% transformation rate, assuming that this rate is sufficiently near to complete transformation, and that the remaining 0.1% of untransformed matter does not have any remarkable influence on the real behaviour. Breakage may happen before the allotropic transformation of a given inclusion is complete, e.g. if it is transformed to 80%. This will happen to big stones in a high tensile stress environment. If, on the other hand, a small stone lies in a low tensile stress region, it will be able to break the glass only when its transformation is mostly fulfilled.

e) The real HST does not work at constant temperature. Therefore, calculation of the breaking rates has to respect the temperature increase from room temperature to 290°C. Calculations with different heating speeds and different NiS species show that even with fast heating (e.g. 10 K/min) and the less favourable limit composition ($\text{Ni}_{0.98}(\text{Fe}_{0.02})\text{S}_{1.01}$), transformation is terminated after reaching a temperature of 255°C (figure 9). This means that, theoretically, a holding time in HST should not be necessary from the point of view of the measured transformation kinetics of the NiS species.

3. Comparison to industrial-scale heat soak tests

Our laboratory trials and scientific calculations do not explain why glass may break during the holding time of the DIN 18516 test [12]. We knew from production personnel that between $1/2$ and about $2/3$ of the breaks already happen during heating, but the remainder break at constant temperature, with a decreasing rate after having reached constant air temperature. An example is

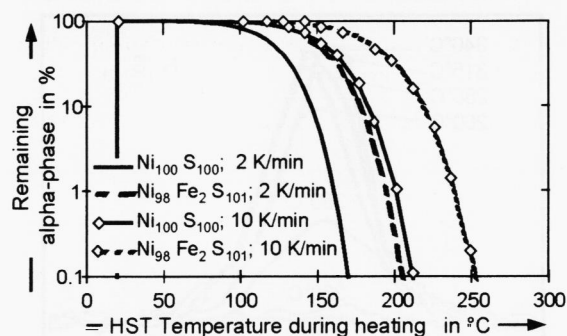


Figure 9. Calculation of the transformation rate of different $\text{Ni}(\text{Fe})\text{S}_x$ species under different heating speeds. After reaching 255°C at the latest, transformation is completed at 99.9%.

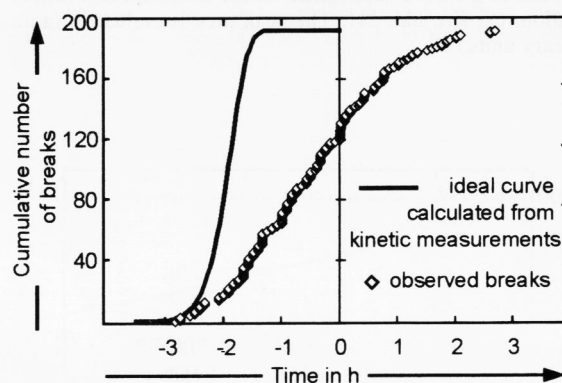


Figure 10. Comparison of the theoretical breakage curve (line) with an example of a breakage curve recorded in an HST oven. Theoretical calculation is for the slowest $\text{Ni}_x\text{Fe}_y\text{S}_z$ composition we synthesised and for a heating rate of 1.29 K/min, corresponding to the real average heating rate of this HST. The difference to the really measured breaks is manifest.

shown in figure 10, comparing the really observed break behaviour to a theoretically calculated curve for the "ideal" HST, using the measured kinetic parameters and the real heating rate of the test furnace. Total number of breaks was 193 in two years. Every HST was carried out over 8 h of holding time (scale ends at 4 h). Later than after about 2.5 h, no break was observed during the entire recording period.

The observed breakage curves show a characteristic S-shape: after a slow beginning, the break rate (i.e. the slope of the curve) comes to a maximum shortly before reaching constant temperature, and then goes back to zero. The S-shape of the curve is principally in agreement with the kinetic calculation, but on closer examination, one can see that even the shapes of the curves are different. Anyway the speed of the real breakage is much slower.

To find an explanation for this obvious difference between theory and practise, we tried to measure the glass temperature during heat soaking. Thermocouples were fixed onto the surface of glass sheets in HST furnaces of different producers and with different loads. It became clear that not every furnace is working well. A typical example will be discussed below in more detail.

Table 2. Breakage frequency in HST. The overall mean value is one break in 6.9 t of glass

sample	tested glass in t	number of breaks	t glass per break
A	2987	292	10.2
B93	1725	372	4.6
B95	2043	300	6.8
B96	2080	275	7.6
B97	2419	383	6.3
B98	2484	344	7.2
C	688	108	6.4
total	14426	2074	6.9

In any case, we were not surprised to find that the glass heats up slower than the surrounding air, and with different speeds in the single points that were measured.

In a first step, we concluded that it is very important to optimise the temperature distribution in HST furnaces to obtain a sufficiently good test result in minimum time.

3.1 Optimisation of an HST oven

In late 1995 and the beginning of 1996, we optimised one of our ovens in order to maximally shorten the test time. Since 1981, this furnace was supplied with a microphone able to detect the time of every breakage. We succeeded avoiding any thermomechanical break (also during heating and cooling) and optimised heating by adapted technical measures. Reality of the breaks was checked by looking for the presence of broken glass in the furnace when a break was indicated by the chart recorder to avoid "blind breaks".

In the time before this work (until 1995), up to 15% of the breaks occurred still after 2 h of test time at constant temperature. After the work, in a time of three years, only four breaks (about 0.6% of the total number of breaks observed) occurred between 2 and 3 h, after 3 h there was none even though the test duration was still 8 h according to the German standard DIN 18516 [12]. So we were rather sure that in this HST oven the break number was complete already after 3 h of holding time.

It is important to obtain a statistically "pure" set of data from the test oven (see below). Optimising our furnace guaranteed to have breaks from nickel sulphide only, and no (or at least a very small number of) breaks due to other reasons for breaking. Only a pure data set can lead to significant results in the sense of high statistical significance.

3.2 Breaking risk of tempered glass sheets

During the last years, we observed the break frequency in our HST ovens (table 2). Over a total volume of more

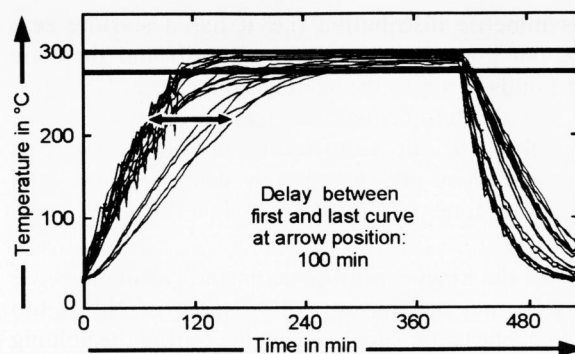


Figure 11. Typical measured heating-up curves of points on glass sheets in HST. The time difference between the hottest and the coolest thermocouple to reach e.g. 230°C is about 100 min.

than 14 000 t of tested glass, we found a mean value of one break in 6.9 t of tested glass. In this number, an estimated 5 to 15% of breaks not due to NiS are included. We suppose this because on the one hand during our research activities, in one explicit case, we found 5.4% of breaks not due to NiS (see section 1), and we assume that this furnace does not produce thermomechanical breaks. On the other hand, in the furnace we optimised, we had found up to 15% of thermomechanical breaks before optimisation. Considering these breaks to be a security reserve, and taking 0.9 t from the mean value of 6.9 t as another security reserve of 13%, we estimate the average breakage risk of untested glass due to NiS to be not more than one in 6 t.

The German standard DIN 18516 is based on a remaining security risk of one break in 400 t of tested glass. This corresponds to a façade with 20 000 m² of 8 mm glass. Consequently, to fulfil DIN 18516, the breaking risk of the HST has to be reduced by $(1 - \frac{6}{400}) = 98.5\%$, which in the following will be called the "sufficient reliability" of the HST. We will also use this number herein in further calculations.

3.3 Probabilistic approach to the break behaviour in HST ovens

3.3.1 Heating-up curves

Measuring the heating-up curves of single points distributed on glass sheets in HST, we remarked that the time delay between the slowest and the fastest of these often exceeded 1 h (example: figure 11). In addition, a delay of about 30 min, compared to thermocouple controlling the process by measuring the air temperature, was found. Evaluating the time necessary to reach e.g. 230°C it becomes clear that the points are aligned following a cumulative statistical distribution curve.

The simplest description by a normal distribution curve is fitting as well as e.g. a Weibull distribution curve. For theoretical reasons, we prefer to use the Weibull function. The normal distribution function is a symmetric distribution (i.e. it comes from and goes to infinity). The Weibull distribution, on the other hand, is

an asymmetric distribution (i.e. it has a starting zero point, but goes then to infinity as well) and therefore corresponds better to the heating-up delays in HST. It is clear that no thermocouple can reach a certain temperature before the air temperature reaches it (starting point), but there may be strongly delayed points even after a long time, thus with a very low degree of probability¹¹⁾.

From the kinetic measurements and calculations, we have seen that the transformation speed of NiS is too high to explicate the breaks occurring during the holding time of the HST. On the other hand, the heating-up curves slow down the whole process, and the estimated delay from e.g. figure 11 is in the order of magnitude requested. So this is the reason why we could apply the Weibull distribution function to describe the breakage data obtained from different HST ovens.

Today we think that heating-up is the slowest process in HST. It is therefore responsible for the apparent kinetics, i.e. the dependence of the break rate on time. The allotropic transformation of the nickel sulphides is so much faster that it does not play a remarkable role.

3.3.2 Weibull distribution function and Weibull statistics

The Weibull distribution function has already been applied very successfully to the description of the bending strength of glass [28]. To apply it to the breakage statistics of HST ovens, the time of every break in HST ovens was recorded by a microphone. We defined the zero point of the time scale to be the time when the oven is reaching constant temperature. Breaks happening before have negative time values; breaks with positive time happened at constant temperature. It is important to arrange the data in this way because a higher loaded oven normally needs more time to heat up, but we are only interested in finding out how long the holding time must be, independently of the heating-up time.

The mathematical calculation steps to be used for the application of Weibull statistics [29 and 30] are relatively complicated. We use a data set of breaks recorded in a Saint-Gobain HST oven (figure 10) in 1996/97 as an example to explain the steps of the calculation.

a) The recorded data are brought to increasing order:

$$t_1 < t_2 < \dots < t_i < \dots < t_{n-1} < t_n$$

(time scale for the abscissa) with n = the total number of events, and i = the current number of an event, and the events are numbered from 1 to n to get the ordinate values. The linear scales plot of these data shows the characteristic S-shape already discussed above.

¹¹⁾ Nevertheless, one should never forget that e.g. the Weibull distribution function is only a model to describe reality. A good fit does not mean that the model becomes reality, but only that the model is able to describe reality in the present case. A certain risk consists always in extrapolating for predicting the behaviour of a given system far over the limit of measured data.

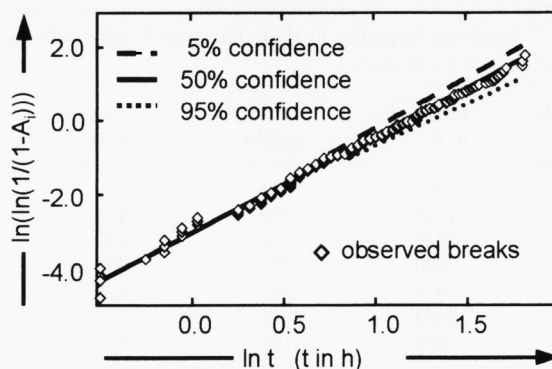


Figure 12. Weibull plot corresponding to the example of figure 9. Every point is well represented by the 50 % confidence straight line, the correlation coefficient being 0.996. Upper and lower lines represent the 5 and 95 % confidence level lines.

b) The ordinate values (i.e. the cumulative number of events) are normalised and transformed using the following function:

$$A_i \equiv (i-0.4)/(n + 0.3) \cdot 100 \% \tag{4}$$

which is recommended in [29]. This transformation is necessary to eliminate zero and 100 % points because of the logarithmic scales to be applied for the plot.

c) Calculation and graphical representation of the Weibull plot of the transformed values A_i (figure 12: abscissa values are $[\ln(t)]$ and ordinate values are $[\ln(\ln(1/(1-A_i)))]$).

d) Check for applicability: The Weibull distribution function can only be applied to a given problem and data set, if and when in the obtained plot all of the measured points are fitted by exactly one straight line. If this is not the case, and apparently the measured points would need more than one straight line (e.g. two parallels or lines inclined to each other), or if the line is curved, Weibull statistics cannot be applied. In our example, the fit is very good with a correlation coefficient near to unity ($R \equiv 0.996$).

e) Two parameters (θ/β) result from the fit line of the Weibull plot calculated following [29]. They characterise the Weibull curve corresponding to a 50 % confidence level ($\theta_{50\%}/\beta_{50\%}$)¹²⁾.

¹²⁾ In terms of statistics, the 50 % confidence level means that when repeating the same trial (e.g. heating-up of the same HST furnace once again with thermocouples at different points), the result will probably be different, but may be higher or lower with the same probability. In other words, one estimates the result of the first trial to be representative. Nevertheless, the Weibull fit line is not in every case identical with the best fit line of the points in the Weibull plot. This is because the weighting of the points is different.

For a great number of events, the 95 and 5 % confidence curves come very close to the best fit line and the 50 % confidence curve, and the latter become identical. Therefore, it is very difficult to identify outliers in a data set of only a low number of points.

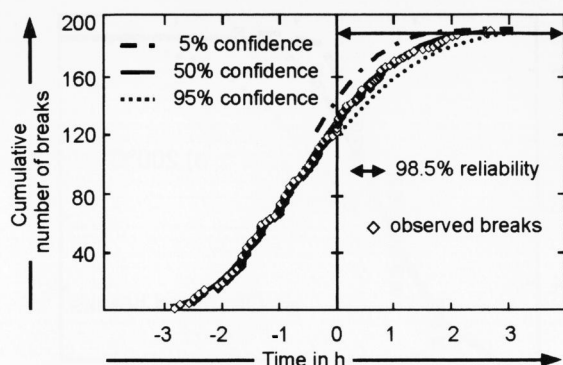


Figure 13. Back-transformation of the Weibull plot of figures 15a and b into linear scales. 5 and 95 % confidence level curves are including every point and the best fit line in a reasonable way. The dotted line represents the 98.5 % level line to calculate what is called the “sufficient reliability” of the HST.

f) For other confidence levels, the corresponding two-parameter sets can also be calculated by a procedure described in [29]. For the statistical evaluation of our breakage problem, we choose to calculate on the one hand $(\theta_{5\%}/\beta_{5\%})$, on the other hand $(\theta_{95\%}/\beta_{95\%})$, to represent graphically the confidence interval in which every break happening in the corresponding HST oven must be observed with a very high statistical probability of 90%. In the Weibull plot of figure 12, this interval is represented by two straight lines, including largely every point of our example data set. This is also an indicator for the applicability of the Weibull distribution function on HST breakage statistics.

g) In a linear scale, and omitting the ordinate transformation following point a), the obtained values (θ/β) are checked by comparing them graphically with the original data set (figure 13). It can be seen that the 50 % confidence curve is fitting the original values very well, and they are included by the 5 and 95 % confidence curves in a reasonable way.

The values for the 5 and 95 % levels are calculated from the number of events represented in the data set. It is clear that for a data set of e.g. only twenty breaks (see table 3) the statistical uncertainty is high. Although if the last break happens only 1 1/2 h after reaching constant temperature, the evaluation of such a data set for the 95 % confidence level does not make sense. We think that for a given HST oven, at least about 50 breaks have to be recorded to get a sufficiently high confidence of the data set.

A higher number, e.g. a data set of 499 breaks, makes the 5 and 95 % limits come much closer to the 50 % confidence curve. This data set in question was recorded in an HST oven similar to that of the first example, so also the results of the best fit curves are very similar (see table 3).

3.3.3 Application of the Weibull distribution to breakage data

From $(\theta_{50\%}/\beta_{50\%})$ and $(\theta_{95\%}/\beta_{95\%})$, one can calculate any point of the corresponding Weibull distribution curves for these confidence levels. We are interested in one special point to fulfil the “sufficient reliability” of the HST as defined above: the time needed to reach a 98.5 % reliability (figure 13). Table 3 shows an overview of the results we obtained up to now in different HST ovens. It is clearly seen that in these ovens, and in the way they are controlled, a holding time of 2 h would normally (50 % confidence) be enough, 3 h would be very safe (95 % confidence).

The extrapolation of the Weibull curve to 8 h of holding time (the duration of the test following DIN 18516 [12]) shows that the breakage risk decreases by over 10 decades (figure 14). Also from this point of view, we can conclude that the test, as it is done today, is much too long.

Table 3. Overview of times to reach 98.5 % reliability in the HST with 50 and 95 % confidence, from different data sets and from literature data. Constant temperature in HST is $(290 \pm 10)^\circ\text{C}$, literature data for constant temperatures are given in column 1. The 50 % confidence level results are comparable to each other because they do not depend as much as the 95 % confidence level results on the number of breaks.

data set	method		observations and remarks
	Weibull 50% confidence time at constant temperature	Weibull 95% confidence time at constant temperature	
no. 1	2 h 19 min	3 h 06 min	193 breaks, $R = 0.996$
no. 2	1 h 54 min	3 h 08 min	108 breaks, $R = 0.995$
no. 3	2 h 10 min	2 h 36 min	499 breaks, $R = 0.996$
no. 4	(1 h 29 min)	(5 h 16 min)	20 breaks only, $R = 0.939$
no. 5	1 h 10 min	2 h 05 min	46 breaks, $R = 0.975$
literature data: laboratory trials with inclusions from industrial glass production			
[14] 200 °C	34 min	55 min	18 breaks, $R = 0.928$
[14] 250 °C	25 min	41 min	15 breaks, $R = 0.954$
[14] 290 °C	≈ 20 min	≈ 30 min	extrapolated values

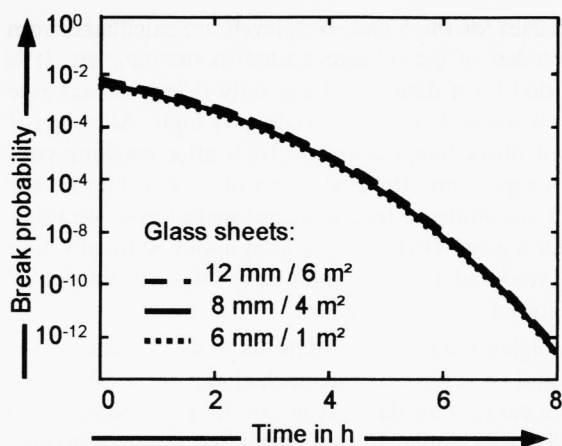


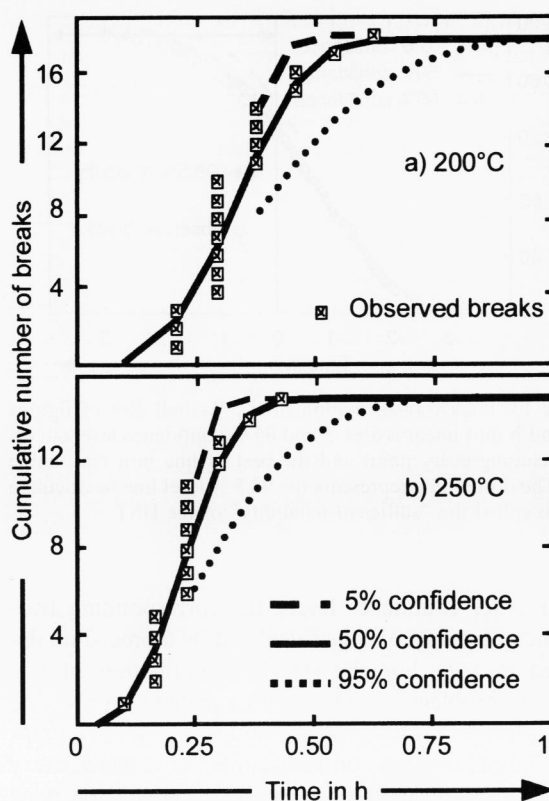
Figure 14. Extrapolation of the Weibull function obtained by fitting HST data from figure 13, for three samples of sheets differing in thickness and surface. The breakage risk is only poorly affected by the dimensions of the sheets, but decreases quickly by over 10 decades during the 8 h of test time following DIN 18516 [12].

It is important to say that the data we are communicating in the present paper have been obtained in very well controlled HST ovens. From our earlier experiences, when measuring the temperature distribution in different test ovens, we know that in some cases the glass was heated up very slowly in several points, in a way that it did not even reach 250°C after 8 h of holding time. We are sure that for such bad tests the above calculated short holding times would not be enough to assure sufficient reliability. We think it therefore to be very important to test each oven with different loads, measuring the temperature distribution on or in the glass and its relation to the process-controlling thermocouple. The beginning of the holding time must be fixed to the moment when all of the glass has reached the test temperature. Long-term behaviour of the oven has to be proven by adapted quality assurance methods.

3.3.4 Application of the Weibull distribution to literature data

The only literature data known by the authors containing breakage times of real NiS inclusions in glass were published by Merker [14]. As already mentioned above, he studied NiS inclusions in drawn glass. In his laboratory oven he recorded the times of the breaks at temperatures of 200 and 250°C, respectively. The samples which did not break were held at these temperatures during at least 2 h. As the last break happened after a total time of only 40 min, we can be quite sure that the number of breaks was complete.

We applied the Weibull statistical evaluation to these data (figures 15a and b) and obtained the 98.5 % values given in the three last lines of table 3. Values for 290°C were extrapolated using the Arrhenius law. In figure 14, it can be clearly seen that there is a time delay of about



Figures 15a and b. Evaluation of literature data (Merker [14]) by the Weibull procedure. Compared to the HST data, breakage is happening very fast, sufficient reliability is already reached after 51 min at 200°C (figure a) and after 36 min at 250°C (figure b) (on 95 % confidence level).

10 min before the first break. This time is necessary to heat up the first NiS stones to minimum transformation temperature in an isothermal environment, which can be compared to the first part of the heating-up time in real HST when breaks have not yet begun.

These results show that in ideal conditions, an HST would not need more than about 25 min (plus cooling phase) to be complete. For real HST ovens, it is clear that this limit value is not yet true. Today's technical standard is such that the glass needs much more time to reach an adjusted temperature, as we showed above. Nevertheless, we are quite sure that the technical process can be optimised to get closer to the time limit shown by Merker's laboratory assays.

3.3.5 An additional security factor: thermal dilatation

As already mentioned above, nickel sulphide and glass possess different thermal dilatation coefficients. This fact also plays a role for the safety of the heat soak tested glass.

The dimension of the cavity in which the NiS stone is located is fixed at T_g (about 550°C for normal float glass). In the HST, glass and inclusion are heated up

again. Consequently, the pressure coming from the transformed inclusion is increased by a term determined by the difference in thermal dilatations. Knowing that the pressure is proportional to the one-dimensional dilatation, and estimating as worst case the theoretical volume expansion of 4 % for the NiS stone, one can easily calculate that by cooling the soaked glass back to room temperature, the pressure of the stone will decrease by about 10 %. In other words, this means that a glass sheet containing an NiS stone which was not able to break the glass in a correctly operated HST (i.e. the transformation is complete, but the NiS is e.g. small or situated in a low-stress zone) will certainly not be broken by this inclusion under normal conditions on a building. In terms of transformation rate, with the same kind of calculation, one can predict that a transformation rate of 92 % would be enough to guarantee the long-time safety of the glass at 80°C.

Consequently, the HST is a safe test. Glass is tested under harder conditions than those that can exist on buildings. If the test is well done, the glass cannot break any more because of nickel sulphide.

4. Conclusions

a) We investigated the kinetics of the allotropic transformation of α to β nickel sulphides by two independent methods. The results show clearly that the transformation speed of really occurring NiS species is fast enough to theoretically be complete during the heating phase of the HST.

b) The typical breaking rate of float glass is one break in 6 to 7 t of glass. Following the German standard DIN 18516 [12], sufficient reliability of the HST is therefore 98.5 %.

c) Real HST ovens do not heat up the glass homogeneously. For the coolest points on the glass sheets, we measured over 2 h a delay in comparison to the air temperature. We think that the heating-up of the glass is the slowest process during heat-soaking, and therefore it deceptively influences the total kinetics of the test. The delays can be described by a Weibull distribution function, also adapted for the description of the bending strength of glass.

d) The evaluation of the break statistics of real HST ovens shows that in a well-controlled HST furnace a holding time of 2 to 3 h is enough to guarantee sufficient reliability. The difference in thermal dilatation coefficients between glass and NiS gives an additional safety. It is nevertheless important to prove the quality of the test ovens by sweeping quality assurance measures. In a badly controlled test oven the transformation of the NiS stones might not be complete.

e) Literature data show that principally the time for heat soaking might be much shorter under ideal conditions. We feel this to be in accordance with our theoretical

kinetic calculations, and we can even hope to shorten HST holding times by better controlling this process in the future.

*

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