# The Significance of Sub-critical NiS Inclusions

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## Abstract

Even after heat soaking, toughened glass is liable to a few apparently spontaneous failures, generally attributed to incomplete conversion of nickel sulphide inclusions. Another alternative is explored here: even with full conversion, inevitably some of these inclusions are too small to fail in the heat soak, but may cause failures at unexpectedly low loads in service. Taking this into account changes the nature of risk analyses for the behaviour of heat soaked glass.

## Introduction

It has been recognised for many years that nickel sulphide inclusions (hereafter referred to as NiS – as usual without meaning to imply precisely 1:1 stoichiometry) can undergo a phase change which involves an increase in volume and may cause failure in toughened glass. In domestic and automotive applications such failures are so unlikely compared with failures due to accidental damage that NiS is not perceived as a problem. However in architectural applications, particularly on high buildings, it is recognised that measures to minimise failures due to NiS are very necessary.

In exceptional circumstances, there may be a safety risk. More commonly, the driving force is the cost of replacement – both the direct cost in situations where access may be difficult, and the indirect cost to the users of the building. Even high rise buildings are not completely free of the risk of accidental or sometimes (sadly) deliberate damage leading to glass failure. Ideally contract arrangements should recognise that there may also be a few ‘spontaneous’ NiS related failures, and take into account the statistical nature of this risk. The safety implications and the possible need for glass replacement have always to be taken into account in designing a building. While it would be desirable to completely eliminate failures related to NiS, to date the glass industry has aimed to limit such failures to one in a few hundred tonnes, ensuring a level below that which must be expected from other causes.

The heat soak test, holding glass at a high temperature for an appropriate period, acts as a destructive test and eliminates a high proportion of the glass which would be liable to break in service. It appears that from time to time unacceptably high levels of breakage have occurred even after heat soaking. Improved understanding of the specification and control of the heat soak process should eliminate such situations – but it remains uncertain what residual level of breakage must still be expected. This paper attempts to provide an estimate of the residual risk.

## Basic Theory

A recent review by Kasper et al [1] provides a very thorough treatment of both the underlying theory and the way heat soak processes have developed. The general idea is that the process should eliminate a specified (large) proportion of the glass which is liable to fail in service. It is assumed that, at least in the later stages of the heat soak when thermal stresses should not be an issue, failures can be attributed to the conversion of NiS inclusions. Such a conversion process is not normally expected to go to completion even at very large times – but it can be taken very close to completion. The use of microphones in heat soak furnaces in recent years to record the times of breakage has been very valuable in determining whether the holding time was about right, too short or too long.

It must be presumed that, with NiS inclusions coming from various contaminants in the raw material or in the furnace itself, and being sensitive to various aspects of furnace operation, the same schedule might not be appropriate for glass from different sources and production dates. However sufficient microphone data is now available to be confident that a heat soak process can be specified which will eliminate a high proportion – 95%, even 99% – of potential failures, at least for all the float glass used in the various published microphone data collection exercises. Potential failures are here defined as those which would have occurred due to NiS conversion if the heat soak had been continued indefinitely. Recent data analysed by Kasper [2] gives reasonable confidence that a heat soak of 2 hours at 290+/– 10C can be expected to give 98.5% of potential failures, and this is proposed for a new standard. This time is considerably reduced from the earlier DIN 18516 – but heat absorbing coatings have always been seen as a particular risk because of the higher service temperature giving faster conversion, and these coated glasses were particularly in mind in setting this standard. The later failures in trials at that time must now be presumed to be related in some way to the coatings rather than to NiS, assuming the intended temperatures were in fact achieved.

It is attractive – but misleading – to assume that the small number of potential failures remaining at the end of the heat soak process are also the potential failures in service, although they may not occur for many years. However it seems clear that the expansion coefficient differential between NiS and glass provides a significant safety factor. The important NiS species are those which remain in the high temperature form after toughening but can convert at service temperatures. Taking the figure quoted in [1], a heat soak which achieves more than 92% conversion should give glass which is free of spontaneous breakage in service. To use this result, it is necessary to relate the number of failures in the heat soak process to the degree of conversion. For this purpose the key formula is that spontaneous failure can be expected for:

$$P \text{ greater than } K / D^2 / S^3 \qquad (1)$$

P is the fraction of NiS converted to the low temperature form.
K is a constant given various material properties of glass and NiS.
D is the particle size – expressed as an equivalent diameter for non-spherical particles, but with NiS being liquid down to glass forming temperatures, the inclusions can be expected to be and generally are close to spherical in the thicker glass used for architectural purposes.
S is the toughening stress, which will vary through the thickness of the glass, with only the tensile stresses towards the centre being of interest.

This formula comes from dimensional analysis using the argument that failure occurs when the stress intensity factor from the stress in the glass is sufficient to continue to grow a crack produced in the (rapidly decreasing) stress field around an inclusion. One of the earliest demonstrations that this argument produces a self-consistent theory in the present application appears in Swain [3]. For the present purpose the value of K does not matter, assuming it to be substantially independent of the glass composition and NiS material properties over the range of interest. Clearly P can not exceed 1, so at any position in the glass spontaneous failure can only occur for D above a critical size Dc proportional to $S^{-3/2}$. At the 98.5% conversion stage of a heat soak (assuming this level is reached), all the inclusions at a given position in the glass with D greater than 1.008Dc will already have caused failure.

If (as can reasonably be expected) the size distribution of NiS inclusions is approximately uniform over the small range of sizes close to the Dc appropriate to various positions through the thickness, it follows that in the heat soak the remaining failures decrease in proportion to the NiS still to be converted. Thus a first order conversion process should result in the number of remaining failures decreasing exponentially with time in the later stages of a heat soak. Without strong a priori expectations, it is hard to be sure of the analytic form of the tail of any experimental distribution where it is necessary to rely on relatively few data points. If the later failures do indeed fit such an exponential curve, its time scale can be used directly to estimate when 92% conversion has been reached. The use of a Weibull plot in [2] to fit microphone data implies the final stages of conversion are faster than expected from a first order process. Fortunately, however the data is interpreted, it seems clear that conversion well above the 92% level can be achieved consistently.

The conversion time in the heat soak appears to be considerably larger than that anticipated from laboratory samples, as discussed in [1], and Kasper et al explore other explanations for the time scale in the microphone data, for example poor furnace temperature control. The microphone data is nevertheless accepted as the only safe basis for specifying standards for a heat soak test, and it is plausible that NiS inclusions formed in a glass melting furnace and embedded in glass behave differently to laboratory samples The important point for the present purpose is that heat soak tests are intended to achieve well above 92% conversion. While the data to confirm they actually did so may have been lacking in the past, that is no longer the case. Thus if a heat soak process is operated to high standards of quality control the problem of spontaneous breakage should be completely eliminated!

However, as in other destructive tests with brittle materials (e.g. mechanical proof testing [4]), despite the heat soak a few pieces may still be unexpectedly weak. Assuming essentially complete conversion has been achieved, inclusions smaller than the value of Dc appropriate to their position in the glass still remain. Allowing for the safety factor from the expansion difference, they can be thought of as having P=0.92 rather than 1. The key theoretical formula (1) then implies that inclusions of size just below Dc will give failure at a stress somewhat greater than S, corresponding to an additional loading of 2.8% of S. At the glass centre S is typically 50MPa, so this additional stress is 1.4MPa. Towards the boundary of the tensile zone where the toughening stress is less, smaller additional stresses could give failure. While design codes vary, and do not necessarily assume a specific failure stress, a typical design stress is in the range 20–30MPa, [5]

What will be referred to as 'sub-critical' NiS inclusions in this paper are then liable to cause failures at additional stresses well below the design loading. Taking into account that the design loading will normally be reached only in bending and at the surface, the tensile zone towards the centre will experience at most half the design load, and that only in extreme circumstances. However smaller thermal and mechanical in-plane stresses of several MPa can develop in many situations, even in the cooling stage after the heat soak. The perceived performance of heat soaked glass may then depend on these low stress failures of fully converted inclusions rather than on truly spontaneous breakage from further conversion. The significance of the loading in failures related to NiS inclusions has been pointed out previously by Jacob [6], but it is examined here from a different viewpoint, and the implications are explored in more detail.

## Breakage Statistics from Sub-critical Inclusions

The stress profile in tempered glass is often close to a symmetrical parabola with zero mean, and this provides a convenient working basis for the present analysis. Taking a co-ordinate y of the distance from the centre line:

$$S = C\,(1 - 3\,(y/h)^2)$$

C is the tensile stress at the centre
h is the half thickness of the glass

The tensile zone extends to y/h = 0.58. In considering failures in the low tensile stress region for y/h approaching 0.58, D may need to be so large that such an inclusion will have been rejected as optically unacceptable. It is convenient to define $D_0$ and $D_1$ as follows.

$D_0$ is the diameter of the largest inclusion to survive the heat soak at the centre, which is here assumed to achieve substantially complete conversion
$D_1$ is the largest D likely to be found

Taking a typical value of $D_0$ to be 75 microns (corresponding to a stress C), and a 500micron defect to be unacceptable, failures in the heat soak can occur only for y/h<0.49. More important, it seems from statistics such as those in Bordeaux et al [7] that inclusions with D larger than 300microns are relatively rare, presumably because unless they are associated with a gas bubble they fall through the glass in the furnace too quickly to go forward into the product. Taking $D_1$ to be 300microns, failures can occur only for y/h<0.45. Other important parameters are the additional stress and the safety factor arising from the differential expansion, which are here defined as follows:

F is taken as the 'safety factor' on P relative to complete conversion, 0.08 corresponding to the equivalent 92% conversion used for illustrative purposes above
L is the additional load, expressed as a stress which is here assumed to be uniform through the thickness

Using these parameters, it is possible to calculate the size range of NiS inclusions which might be expected to cause failure in service – here assumed to occur the first time the load is reached after the heat soak.

The largest, $D_{max}$, is the smaller of $D_0 / (1 - 3\,(y/h)^2)^{3/2}$ and $D_1$
The smallest, $D_{min}$, is the smaller of $D_0$ / (1–F)**1/2 / $[(1+L/C - 3\,(y/h)^2)]^{3/2}$ and $D_1$

For very small L the calculation is slightly complicated by there being no failures in service at the centre, i.e. $D_{min}$ is greater than $D_{max}$ at y=0. However in view of the above discussion this requires L below 2MPa, a level which can easily appear very early on in handling and storage: in the range of most interest from say 2MPa to 10MPa this complication does not arise. However in order to make use of the result it is necessary to know how many inclusions are present in the size range of interest. It appears from the data in [7] that the size distribution of NiS particles is roughly uniform with size up to the 300micron cut-off, at least from the lower limit of detection. The argument is developed further here on this basis, and current evidence suggests it is an adequate basis for risk analyses. The number of potential failures in service from sub-critical inclusions can be calculated in terms of the number of NiS inclusions in the glass taking:

N as the total number of NiS inclusions per tonne (assumed uniformly distributed through the glass thickness, and also uniformly distributed in size up to $D_1$ – with 300microns as an appropriate value).

First calculating the expected number of NiS related failures in the heat soak, this amounts to:

$\int N\,(1 - D_{max}/ D_1)\,dy/h$ which can be expressed as:
$N/\sqrt{3}\ \ (1 - (D_0/ D_1)^{2/3})^{3/2}$ per tonne

In the situation of interest when L is large enough to ensure some additional failures occur at the centre, requiring:

$L/C > 1 + 1/ (1-F)^{1/3}$ and taking also:

$A = (1 + L/C)\,(1 - F)^{1/3}$

the additional failures amount to:

$\int N\,(D_{max}/ D_1 - D_{min}/ D_1)\,dy/h$

which can be expressed as the following fraction of the number in the heat soak:

$[(A - (D_0/D_1)^{2/3})\ \ / (1 - (D_0/D_1)^{2/3})]^{3/2} / A\ -\ 1$

In using this result, it must be remembered that a change in C will also change D0 in accordance with (1). If the conversion is not quite complete in the heat soak process, the value of the safety factor F is effectively reduced – but the potential failures at a given service load will not all occur until conversion is complete, perhaps after some years in service. Again taking D0 to be 75 microns for illustrative purposes, with C as 50MPa and F of 0.08 the expected NiS related failures are as follows:
0.7% of those in the heat soak for L of 2MPa when A = 1.005
5.3% of those in the heat soak for L of 5MPa when A = 1.070
23.6% of those in the heat soak for L of 10MPa when A = 1.167

In interpreting these figures, it must be remembered that in most loading situations the highest stress occurs only in a limited region, while in the heat soak the whole area is affected. A factor of 1/3 is included in the conclusions below. Further the weakest glasses may fail even in the cooling phase of the heat soak, or in handling. In some cases, even without actual mishaps, the glass may experience a substantial proportion of the design stress before it is installed.

A 'successful' heat soak is regarded as eliminating all but perhaps 1.5% of the potential failures, but the basis of this estimate is open to dispute. However for entirely different reasons the above figures indicate that from the customer's point of view this level of premature (but not strictly spontaneous) failures may well arise as the loading approaches the design value. Around the design value, when failures are still expected to be infrequent, in some situations a surprisingly high proportion may be related to NiS. To take full advantage of the reliable performance which can now be expected of the heat soak process, in critical applications a further proof test (most simply a thermal shock by immersing the glass in a hot liquid) might be envisaged to eliminate the 'sub-critical' inclusions.



## Conclusions

- Enough is now known to be reasonably confident that the Heat Soak Test can be operated to avoid the risk of spontaneous breakage.
- However some remaining 'sub-critical' inclusions may still give breakage below the service load, even if they are fully converted.
- The residual risk can be evaluated using microphone data from the heat soak test.
- The required data may be taken for the industry as a whole, or for a particular production operation – if sufficient data is available to distinguish it from the norm.
- It appears that at normal handling and operating stresses these sub-critical inclusions might give 2% of the failures experienced in the heat soak, but as conditions reach the design load this figure rises to perhaps 8%.
- Overall, more consistent heat soak operation should avoid major problems of spontaneous breakage, but the customer will continue to see some unexpected failures, especially when the glass experiences a significant load.
- In particularly critical applications a further thermal shock test might be used to eliminate these sub-critical inclusions.

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