Glass breaks

from nickel sulfide inclusions

Scholars explore why

By Abhi Ray and Leon Jacob

nterest in nickel sulfide inclusions in glass dates to the 1960s. In recent years, theoretical studies on the phase changes in nickel sulfide from a combination of thermal analyses, X-ray powder diffraction and Raman spectroscopy using reagent-grade chemicals, have provided significant insight into its transformation behavior in laboratory conditions. The glass industry's attention has focused on both the failure mechanisms of toughened glass panels containing nickel sulfide inclusions and the search for post-processing remedial methods. This paper reviews both theoretical and practical aspects of dealing with nickel sulfide in toughened glass and proposes a two-stage heat treatment model to ensure recrystallization followed by growth of ß-nickel sulfide grains from the precursor α- nickel sulfide polycrystalline inclusions.

The problem at hand

Toughened or tempered glass panels as glazing material proves vulnerable to fracture if nickel sulfide inclusions are present in them prior to toughening. Although the number of reported failures of these safety-glass panels is small partly due to worldwide efforts by practitioners and researchers, toughened glass still remains a focus of attention due to its potential fracture in an unpredictable manner.

The origin of nickel sulfide inclusions in glass is yet to be understood fully. A number of sources of nickel and sulfur including contamination of glass by nickel from alloys such as thermocouples, stainless steel feeders, addition of nickel oxide as a colorant and sulfur compounds used as refining agents have been suggested. Similarly, a number of mechanisms of the formation of nickel sulfide have also been proposed. For a list of references to this study, see the conference papers presented at Glass Processing Days in Tempere, Finland, June 17-20, 2005, where this research was originally presented.

Of the various forms of nickel sulfide, the slightly nickel deficient form ($Ni_{1-x}S$), stoichiometric from (NiS) and nickel-rich form (Ni_7S_6), are generally regarded as potentially dangerous with respect to fracture of toughened glass. There is general agreement with regard to the mechanism of fracture of toughened glass containing nickel sulfide inclusions, and the fracture is believed to be related to the phase transformation of the metastable α- to the thermally stable, ß- form which is accompanied by a substantial (4 percent) increase in volume.

Heating soaking

In recent years, much debate has been centered on the effectiveness of heat-soaking tests to reduce or eliminate the failure of toughened glass containing nickel-sulfide inclusions.

Differences in opinion exist with regard to both the maximum temperature of soaking as well as the time necessary at the maximum temperature. Recommendations on the heat-soaking process are being made for incorporation in major standards. For instance, in the European standard EN 14179-1, a soaking at 290 degrees Centigrade, plus or minus 10 C for two hours is prescribed for toughened building glasses to prevent nickel-sulfide-induced failures. The implied residual contamination after heat soaking of one nickel-sulfide inclusion in every 4,000 tons of heat-soaked glass can be misleading for the consumer. Specifications recommending heat soaking in the EN 14179-1 standard fail to recognize that the implied residual contamination does not apply to any specific project, but rather to

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a specific heat-soaking furnace for a whole year's production. Past studies have shown that contamination levels vary significantly and, therefore, can result in a higher residual contamination level after heat soaking.

This paper reviews some of the recent theoretical studies on the phase transformation in nickel sulfides and experimental investigations with the heat-soak test. It highlights the differences in the recommended temperature and duration of soaking. A case for a two-stage soaking process is presented for consideration.

Theoretical study

For the past 40 years, a number of studies related to nickel-sulfide inclusions in glass have been carried out to understand both the polymorphic phase transformation in nickel-sulfide compounds and failure mechanisms related to some of these transformations. For instance, researcher M.V. Swain discusses the critical size of nickel-sulfide inclusions found in both annealed and tempered glass and concludes that th critical size in tempered glass—different from that in annealed glass—depends on the location of the inclusion and the tempering stress within the glass. Swain's predicted diameter of nickel-sulfide inclusions to cause spontaneous failure in tempered glass is in accord with what is generally observed in real-life failures.

More recently, theoretical studies have been carried out at the University of Technology in Sydney, Australia, by D.W. Bishop and other scholars, using a variety of analytical techniques including thermogravimetry, differential scanning calorimetry, X-ray diffraction and Raman Spectroscopy. High-purity nickel sulfide powder, confirmed by X-ray diffraction as ß-NiS, was studied using differential scanng calorimetry between 35 C and 450 C. Thermogravimetry data revealed a transformation of Millerite to Godlevskite (Ni_7S_6), indicating a change in composition from a stoichiometric NiS starting composition to a sulfur deficient form within the experimental regime. It is worth mentioning that the sulfur deficient Godlevskite (Ni_7S_6) is known to undergo ß-α phase transformation at 397 C. Earlier, E.R. Ballantyne made an interesting observation that NiS of higher sulfur content was present in failed glass containing nickel-sulfide inclusions. Thus, it seems possible that spontaneous failure of tempered glass containing nickel-sulfide inclusions may not necessarily be due to stoichiometric NiS. Sulfur-deficient or sulfur-rich varieties also could play an important role in the fracture of glass during its transformation from a metastable high-temperature form to a more stable low-temperature form.

Using the DSC technique, Bishop and other researchers observed that the kinetics of the α-ß transformation in Godlevskite, which was readily obtained from the decomposition of Millerite, were of the first order. The value of the activation energy calculated for the transformation of α to ß, was found to be relatively low and the rate equation predicted a transformation in the order of a few years at ordinary temperatures. They also commented that the transformation times for higher sulfur content NiS would be reduced and would therefore induce failure of tempered glass in shorter times than for the sulfur deficient Godlevskite variety.

In a later report, Bishop and others proposed a two-stage kinetic model for the α-ß, phase transformation in NiS using differential scanning calorimetry under isothermal and non-isothermal conditions. The two-stage transformation model comprised of an induction period followed by a transformation step and the total times of transformation using this model were calculated to be of the order of 120-to-300 days. These values are in good agreement with those observed for failures of installed glass panels, thus reinforcing the value of fundamental studies to derive predictive models for real-life problems.

In a series of publications, A. Kasper and his coworkers have carried out critical measurements of nickel-sulfide phase transformation kinetics. From experimental evidence, Kasper has commented on the importance of a very low heating rate to necessitate the formation of germinated crystallites that will ensure the α to ß, transformation. The experimental evidence has formed the basis for recommending the heat-treatment schedule with a low heating rate and a minimum temperature of 280 C but below 300 C.

Heat soaking of tempered glass

In recent years, much has been written and debated about the heat soaking of tempered glass as a measure to eliminate nickel-sulfide induced failure of installed glass panels. Heat soaking is essentially aimed at inducing spontaneous breakage in tempered glass containing nickel-sulfide inclusions prior to its use as a glazing material. While heat soaking has been used by the industry for more than 30 years, the fundamental reasons behind its effectiveness are yet to be fully understood. Even after many trials by researchers in different countries, there remains considerable disagreement regarding the recommended temperature of soaking as well as the heat-treatment regime to be followed to have a desirable outcome.

In some cases, glass manufacturers have provided strong arguments in favor of the positive effects of heat soaking, pointing out that it can definitely reduce the probability of nickel-sulfide induced fracture of flat glass. Equally, questions have been raised regarding whether the heat-soaking method of protection can be justified from a cost viewpoint, considering that the percentage of failure of tempered glass due to nickel-sulfide stones is extremely small. The debate surrounding heat-soak testing with regard to its ability to totally eliminate the presence of the metastable, α- form of nickel sulfide still remains and also has been extended to the temperature regime to be employed.

Kasper's review, in the 2001 GDP proceedings and elsewhere, provides an excellent insight into the theoretical and practical aspects of the heat-soaking process with regard to the nickel-sulfide problem in tempered glass. The novel use of microphones to record the number of breaks during the heat-soaking process provided valuable statistical evidence of the overall success of the process, and an estimation of the duration of the soaking required to have sufficient confidence in the process. In another paper, Kasper has argued that at 290 C plus or minus 10 C for two hours of heat-soaking for tempered glass is capable of eliminating more than 98 percent of potential failures. The European Standard EN 14179-1 was proposed following these investigations.

D. Gelder discusses the residual risk involved in the heat-soaking process of tempered glass containing nickel-sulfide inclusions and concluded that even after heat soaking, some "sub-critical" inclusions could potentially cause breakage below the service load. His study suggests that "sub-critical" inclusions could account for 2 percent of failures even after heat soaking, and this figure might be higher, depending upon the design-load environment. Gelder believes that customers of tempered glass will continue to experience unpredictable failures of tempered glass under significant load and suggested that a further thermal-shock test could eliminate the "sub-critical" inclusions.

Following their experimental investigations, researchers C. Sakai and M. Kiuta proposed that the

Little monsters

By Bill Marchitello

In London during November 2004, a building under construction repeatedly made headlines when reporters declared it had "glass cancer."

Contractors investigated the soundness of all the internal panels on this fully glazed Greater London Authority headquarters near Tower Bridge after finding many broken panes. Analyses suggested that one cause of breakage was nickel-sulfide stones.

In November 2005, nickel sulfide was again considered culprit by technicians studying glass breakage at Millennium Point, a Birmingham science museum and theater in the United Kingdom.

Nickel-sulfide stones in glass seem to be a perpetual problem. Due to their minute size, when glass is heat treated, nickel sulfide stones become cause for concern.

Don't say, 'so what'

Not too long ago, some glass breakage was considered normal because of the stress incurred when tempering glass. Spontaneous breakage also was considered normal due to edge damage and scratches compounded with size and wind-load stresses.

Fabricators, contract glaziers and glass-shop owners now enter a construction arena with much higher stakes. The replacement dollars add up faster when high-performance glass breaks after being installed in sophisticated, high-tech and custom settings. Therefore, when planning glass applications with architects designing skylights, point-supported walls and high-rise buildings, for instance, all options should be considered to reduce the chance of breakage after installation. Compare heat-strengthened glass versus tempered glass, and tempered glass versus tempered and heat-soak tested glass. Carefully weigh the options.

Developers, general contractors and consultants should be made aware of the possibility of spontaneous breakage and nickel-sulfide stones when specifying tempered glass. Do your part: attempt to inform as many people as you can connected with developing projects and deciding on the products to use. If specifiers are informed, they can't plead ignorance.

If the choice is heat-strengthened glass, the risk of breakage from nickel-sulfide stones becomes negligible. If there aren't any security issues surrounding the building, heat-strengthening—at low temperatures for a brief amount of time—emerges as the way to go.

Tempering glass at higher temperatures for longer times remains a fine option because of impact resistance and improved security. However, if there is a concern with breakage, heat-soak testing becomes critical.

Nine years ago, managers at Prelco, a Riviere-du-Loup, Quebec, Canada, fabricator, decided to meet the demands of owners and architectural specifiers of tempered glass by heat-soak testing its products. The market demanded this measure. Even on jobs where most of the building called for annealed or heat-strengthened glass, if you couldn't heat-soak test the tempered glass, you lost the opportunity to quote the job.

Prelco's executives got the message early and purchased the equipment to do the heat-soak test.

During a heat-soak test, tempered glass is heated to about 290 degrees Centigrade for a specific period of time and cooled gradually. During this process, the nickel sulfide expands and glass with stones usually breaks. This detection process dramatically reduces job-site breakage. Unfortunately, this exercise doesn't guarantee 100 percent elimination of all spontaneous breakage, but it does identify problem batches with nickel sulfide.

People in the glass industry take breakage from nickel-sulfide stones as a matter of course. They don't realize that the whole industry suffers when the noisy crack of broken glass, heightened by media exposure and powerful words such as "cancer," makes waves around the world. More widespread use of heat-soak testing of tempered products can help alleviate the potential damage.

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perfect reduction of nickel-sulfide stones and their further phase transformation could be achieved by a combination of oxidizing agent additions, such as zinc sulfate or nitrate, to the glass melt and heat-soak testing. Interestingly, their model suggests a maximum temperature of 260 C for heat soaking, some 30 C less than that suggested in Kasper's model. It should be mentioned that Sakai and Kiuta's model, first presented at GDP in 2001, considers a non-pure nickel-sulfide composition and is thus not directly comparable to Kasper's model with regard to the maximum temperature for heat soaking.

From the preceding discussion, it is clear that despite serious efforts made by the glass manufacturers during the last few decades, nickel-sulfide stones, unfortunately, still occur in architectural and automotive glass, and, after toughening, problems related to unpredictable cracking of nickel sulfide containing glass due to α-ß, phase transformation are still reported.

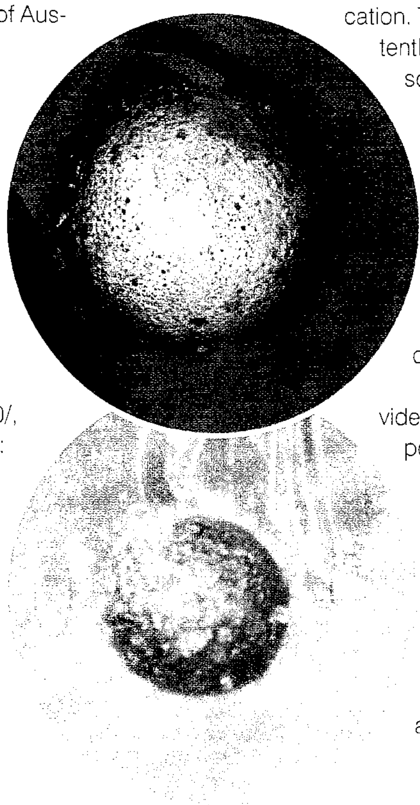
There is little doubt that glass manufacturers will continue their efforts to totally eliminate nickel-sulfide stones in glass and, if a full-proof solution is found, toughening of nickel-sulfide-free glass can then be carried out without the fear of unpredictable failure at a later date.

While oxidizing agents such as zinc sulfate hydrates, zinc nitrate hydrates, other metal salts or metal compounds may have the potential to effectively reduce the formation of nickel sulfides in molten glass, the fundamental problem with the penetration of oxygen to preferentially oxidize nickel or sulfur in nickel sulfides in a highly viscous silicate melt will be the major hurdle for the manufacturers. In other words, toughened glass containing nickel-sulfide inclusions, however small the numbers might be, can still be expected by the community. Additionally, it is difficult to comprehend that toughened glass will lose its appeal to the designers for specific applications where safety and strength are a major issue.

To date, heat soaking has proven to be an effective post-toughening method from the viewpoint of nickel-sulfide related failures. Future development of new standards for safety glass in different parts of the world will be based on sound experimental evidence as well as real experience with toughened glass. In this context, it is important to highlight the noted difference in recommendations for the maximum temperature for heat soaking of toughened glass as well as the holding time at maximum soaking temperature.

For instance, it may be argued that if less than 30 minutes at 260 C is adequate for perfect reduction of nickel sulfide in toughened glass, as cited by Sakai and Kiuta, why is it necessary to soak the glass for two hours at 290 C (Kasper), which seems to the favored recommendation for the European standard EN 14179. The possibility of the presence of impurities of metals other than nickel in nickel-sulfide inclusions in normal soda-lime-silicate glasses can-

Photoglass process to detect nickel sulfide



John C. Barry, principal, PicaMS Pty Ltd. of Australia, worked in conjunction with Resolve Engineering of Australia, to develop a patented method, called Photoglass, for on-site detection of nickel-sulfide inclusions in glass windows. The method was developed in a partnership between The University of Queensland and Resolve. Using Photoglass, 291 nickel-sulfide inclusions were detected in 281 windows in a Brisbane building in 1995-96.

According to the GlassOnWeb site, at www.glassonweb.com/articles/article/330/, the Photoglass process has three stages: photography, film examination and glass inspection. In the first stage, the windows are photographed using wide-format—120-millimeter roll film—cameras with tilt lens and special fine-definition film.

In the second stage, the films are examined in modified microfiche readers with film examiners at nine times magnification. The microfiche readers are modified to consistently scan the film, one frame at a time, and relate scan position to position on the film, according to the GlassOnWeb article.

When film examiners find a characteristic pattern, known as a "dot pair," they enter its position-in-film into a database. This database relates position-in-film to the actual position-in-glass. The "dot-pair" images are generated by inclusions in glass and the spacing of the dots is used to measure the depth in glass of the inclusions.

In the third stage, window examiners, provided with lists of the suspect inclusions, use the positions in glass as provided by the database to locate the small inclusions and examine them with a lupe eyepiece with a magnification of 10. At this magnification, nickel sulfide inclusions are easily identified from their golden-brown color and rough surface texture, the researcher states.

The Photoglass method is rather labor intensive, however, it is technically possible to automate it, according to the Internet site.

not be ignored and, if such impurities are present, then a decrease in the eutectic temperature of phase transformation from α- to ß-nickel sulfide is feasible. For instance, the effect of excess sulfur in the case of other metal impurities will change the stoichiometry of NiS to $Ni_{1-x}S$ and might reduce the transformation temperature of α to ß from a high value to below 282 C.

Given that nickel-sulfide stones in glass occur as polycrystalline inclusions, the transformation of α- to ß-nickel sulfide may be viewed as a case of recrystallization and grain growth where new generation, strain-free ß crystals are produced upon heating.

In the model proposed below, the term grain growth is meant to indicate the increase of the average grain size of strain-free grains without a change in the overall grain size distribution arising from primary recrystallization. Under isothermal conditions, growth generally occurs after an induction period and the rate of growth is usually linear. During the induction period, stable nuclei are formed, and because the nucleation rate increases with temperature, the induction period will decrease as the temperature of isothermal soaking is increased. It follows, therefore, that at a higher temperature (290 C) the soaking time should be less than at a lower (260 C) temperature, but the opposite has been recommended by the experimentalists. Here, I cite Kasper's recommendation of two hours at 290 C against Sakai and Kiuta's 30 minutes at 260 C. Additionally, both recommendations imply that nucleation of ß-nickel sulfide from the original α-form and the subsequent growth of ß-form will take place at isothermal conditions where the temperature is kept constant at either 290 C or 260 C.

While these isothermal conditions may be considered to be sufficient for the nucleation of ß-nickel sulfide crystallites, it is possible that some of the nuclei might not be large enough to be stable and may revert to their original α-form. This may create an environment where not all α-nickel sulfide will transform to the stable ß-form.

Two-stage recommendation

In view of this apparent difference in both the soaking time and maximum temperature of soaking, we propose a two-stage heat-soak method for consideration. Our two-stage model is similar to what is already well-known in the glass industry for the production of glass ceramics where the heat-treatment schedule includes a lower temperature for nucleation followed by a higher temperature for growth of nucleating crystals.

In glass ceramics, efficient nucleation is the key to the successful manufacture of the article and the nucleation process is heterogeneous where crystals grow on particles of deliberately added nucleating agents.

A toughened glass containing α-nickel-sulfide inclusions may be considered in a similar light where α-nickel sulfide can be considered to play the role of nucleating agents in glass ceramics. If this toughened glass is heated to the temperature where ß-nickel sulfide will nucleate, and following the nucleation of ß-nickel sulfide, the temperature is increased where the growth of ß-nickel sulfide grains will be facilitated. Our proposed model of heat-treatment process for toughened glass containing nickel-sulfide inclusions does not assume that both nucleation of ß-crystals and their growth take place at the same temperature and is therefore, more in accord with the known theory in glass technology.

The heat-treatment schedule will need to be optimized experimentally to achieve the desired effect in the toughened glass. In other words, either all existing α-nickel-sulfide crystals in the polycrystalline inclusion will be totally converted to the stable ß-nickel sulfide to assure future safe performance, or cracked glass due to expansion related transformation from α-form to ß-form during the heat-treatment process will be readily identified and rejected. At this stage, without the benefit of extensive experimental work with respect to the temperatures of the proposed two-stage process, and with the constraints of not exceeding 300 C during heat soaking to avoid de-tempering of the glass, it is difficult to recommend with confidence the recrystallization and growth temperatures. However, existing knowledge from experimental work carried out will point to a nucleation temperature of around 260 C followed by the growth temperature of 290 C as have been indicated with sufficient confidence by Kasper, Sakai and Kiuta. This will ensure that the ß-nickel sulfide crystals once formed will have the opportunity to grow to sufficient size and not transform back to the α-form like dissolved embryo.

With regard to the soaking time at either the nucleation or growth temperature, again, experimental proof is needed to recommend the duration period with any confidence. Nevertheless, it is difficult to see why a longer period at the growth temperature (290 C) will be required than that at the suggested nucleation temperature (260C), if, as proposed by Sakai and Kiuta, 30 minutes at 260 C is sufficient for recrystallization. Hence, a 30-minute soaking time for both nucleation and growth temperatures may be sufficient to achieve the desired results.

Conclusions

It is proposed that a two-stage heat soaking at two different temperatures be considered to enhance the reliability of the heat-soaking process in relation to nickel-sulfide induced toughened glass failures. Carefully conducted experimental work is needed to optimize both the temperature of soaking and the duration of soaking in isothermal environments.