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Behaviour of Nickel Sulphide Inclusions in Glass Melts

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Abstract

A brief review of the magnitude of the nickel sulphide problem is discussed. Nickel sulphide inclusions have been studied in soda-lime annealed glass and SLS tempered glass. The discussion was meant to clarify the cause for appearing nickel sulphide inclusions in glass, and explain how these inclusions may cause tempered glass to break. Since these inclusions cannot be eliminated, the discussion addresses how to reduce the potential of nickel sulphide inclusion breakage. The glass batches with different source of nickel sulphide were melted in the laboratory conditions, as well as glass with metallic nickel addition was prepared. The possible forming process of nickel sulphide in glass was tested. The DTA/DSC, XRD, SEM studies allowed us to state that the formation of inclusion from nickel and sulphur during the manufacturing process is difficult, moreover in some cases not possible. The nickel sulphide was introduced to SLS float glass and then tempered. The tempered glass samples, which included the NiS stones, were investigated by microscopic (SEM) method and characterized by EDAX analysis. The glass samples were analysed by elastooptic studies. The obtained results will help to solve the problem of forming nickel sulphide inclusions.
Keywords: NiS, Tempered glass, SLS glass

REDUKCJA INKLUZJI SIARCZKU NIKLU W SZKLE

W artykule podsumowano badania dotyczące pojawiania się w szkłach inkluzji siarczku niklu. Inkluzje badano w odprężonych szkłach sodowo-wapniowo-krzemianowych oraz w szkłach hartowanych. Przeprowadzone badania mają na celu wyjaśnienie przyczyn powstawania inkluzji NiS oraz mechanizmu pękania szyb hartowanych zawierających inkluzje. Podjęto próbę redukcji inkluzji NiS w szkle. W celu zbadania mechanizmu tworzenia siarczku niklu w szkle wytopiono składy, do których wprowadzano NiS przy użyciu różnych surowców. W badaniach wykorzystano metody DTA/DSC, XRD, SEM. Szkła zawierające NiS poddano procesowi hartowania, a następnie analizowano przy pomocy mikroskopii skaningowej SEM/EDAX.
Słowa kluczowe: NiS, szkło hartowane, szkła SLS

1. Introduction

The problem with occurrence of defects in the form of nickel sulphide inclusions during manufacturing float glass panels was announced for the first time in the year 1960 [1]. Although nickel sulphide inclusions occur rarely in soda lime glass (SLS) in the amount of 5 μg per tone (mean concentration of 5 particles per 1012 kg), their elimination is still not solved [1]. Nickel sulfide is a crystalline compound, occurring in two allotropic forms, *i.e.*, high and low-temperature form. The low-temperature phase β-NiS is stable below 390°C, whereas the high-temperature phase α-NiS is stable above the mentioned temperature [2, 3]. Such inclusions are not dangerous if glass panels, in which they occur, are not subjected to the tempering process.

The problem arises, when a panel with the nickel inclusion is tempered, *i.e.*, exposed to thermal processing aimed at the formation of the characteristic stress system, resulting in a mechanical and thermal strength increase [2-5]. Tempering is accompanied with heating the glass up to possibly high temperature, followed by fast cooling.

In the first stage of rapid cooling, with use of the air blower, the hot glass is exposed to the transformations. Shrinkage of the surface layers takes place in the first stage. The layers loose their ductility and they compress external layers of the hot glass. Tensile stresses developed in external layers and compressive stresses formed in internal layers are generated in this phase [6, 7].

Inversion of the stresses takes place in the second stage. In the middle zone, the glass continues cooling, but it cannot shrink properly, because of the rigid external crust. As a result, tensile stresses are developed within external layers of the tempered object, and compressive stresses within its internal layers. At the same time, volume of the tempered object is not reduced. A stresses inversion time depends on cooling rate and heat properties of the glass in question [8, 9]. Nickel sulphide occurring in such panel is „frozen" in high-temperature form, which is characterized with smaller volume as compared with low-temperature form. High-temperature form α-NiS constitutes meta-stable phase in room temperature, and it tends to be transformed into stable form β-NiS in such conditions. Considerable volume increase is observed during this transformation [10]. The process in question is elongated in time and it can cause glass fracturing even after few years of exploitation. It is very hazardous phenomenon as the glass panel with invisible faults can be fractured after some time in result of permissible strength exceeding. Particularly high probability of the panel destruction can be expected when nickel sulphide particle occurs in tensile stresses activity zone, as the glass is even eight times more resistant to compressive stresses than to tensile stresses [11].

1.1. Nickel sulphide in silica-lime-soda flat glass

Based on the literature we can conclude that various types of nickel sulphide inclusions can occur in glass. According to Tabuchi, there are three various types of nickel sulphide inclusions in glass. The first and the second type of nickel conclusion of a formula Ni_3S_2 does not cause spontaneous fracturing of tempered glasses, whereas compound of the composition similar to NiS can cause spontaneous fracturing of glass panels. It was proved that the composition of nickel sulphide inclusion ranges from Ni_7S_6 to $NiS_{1.03}$. However, these inclusions are not composed of a single phase, but they can comprise several phases as: Ni_7S_6, Ni_2S_3, Ni_9S_8 and $Ni_{1-x}S$ H [12, 13]. The temperature of transformation of the $\alpha \rightarrow \beta$ form, is changed in dependence on the sulphur content in the nickel sulphide [13]. Kasper and Stadelmann have proved that nickel sulphide can survive as the meta-stable phase in the glass containing metallic nickel; thus in production of soda-silica-lime glass, we should avoid contact between nickel alloys and the raw materials used [14-17].

1.2. Sources of nickel sulphide in silica-lime-soda flat glass

As nickel melting temperature amounts for about 850°C, we can expect that nickel sulphide can be synthesized during flat glass manufacturing with use of the float method.

Origin of sulphur occurring in the glass mass is generally known, as the sulphur is added into the set mostly in the form of Na_2SO_4 (sulphate), as refining agent. Moreover, sulphur is present in gases used in a glass melting furnace. However, the nickel origin is not fully explained, mostly because of a large number of potential sources of its release. Analysis of the flat glass production line structure suggests that the raw material silos, scales, mixers, burners, measuring apparatus housings and coolers are built of the nickel containing steel. Such steel, in spite of high resistance to corrosive environments, are not sulphur resistant at high temperatures. This leads to the formation of sulphide products on the steel surface, including nickel sulphide.

Refractory materials can be the next source of the nickel release. Components of these materials enter the molten set as a result of corrosive action of the glass mass and high temperature. Studies on chemical composition of furnace oil used in melting kilns proved that the oil contains nickel trace amounts. Replacement of furnace oil with the natural gas and application of containers and burners made of better materials improved the situation, but the problem of spontaneous fracturing the tempered glasses was not fully solved [13, 16].

2. Experimental procedure

A part of tempered glass from the building elevation, which fractured spontaneously without of intervention of mechanical factors, was exposed to macroscopic observations. Chemical compositions of glasses were designed in order to study the mechanism of nickel sulphide formation in flat glass. Chosen materials introducing nickel (Ni) (Table 1) were applied apart from the standard raw materials used in a melting process. Prepared batches were melted in an electric furnace at a temperature of 1450°C, in which the reductive atmosphere was obtained via the graphite introduction. The molten batches were poured out onto a steel plate and annealed at a temperature of 500°C. All molten glasses were exposed to macroscopic assessment with use of a magnifying glass, as well as to microscopic assessment by use of a scanning electron microscope (SEM). The glass samples with inclusions were exposed to EDAX analysis.

Table 1. Compositions of molten glasses.

Raw material	Glass composition [g]			
	Glass 1	Glass 2	Glass 3	Glass 4
Sand	60.63	60.63	60.63	60.63
Dolomite powder	14.82	14.82	14.82	14.82
Magnesite	0.58	0.58	0.58	0.58
Sodium sulphate	1.31	1.31	1.31	1.31
Soda	22.54	22.54	22.54	22.54
Aluminium oxide	0.71	0.71	0.71	0.71
Potash	0.28	0.28	0.28	0.28
Metallic nickel	0.50	1.70	-	0.025
Nickel file dust	-	-	0.025	0.04
Sulphur	-	-	0.5	0.5

In the next step, six identical flat glass panels of 3 mm thick were prepared. On three panels, in the middle, synthetic NiS was placed in the amount of 0,05 g, then the panels with NiS were covered with three glass panels forming a "sandwich". That allowed entrapping the NiS between two layers of flat glass. Such a way prepared panels were melted in the electric furnace at the temperature of 1050°C. After annealing, three flat glass samples in the form of 6 mm thick plates with nickel sulphide inclusions were obtained. Based on XRD phase analysis, the presence of NiS inclusions was proved. The samples were tempered. Then the experiment described above was repeated for adding small amount of zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$) into the nickel sulphide. The samples were melted in the furnace, then annealed and exposed to the tempering process. The phase composition of the developed inclusion was determined by use of XRD and SEM, and the samples were tempered.

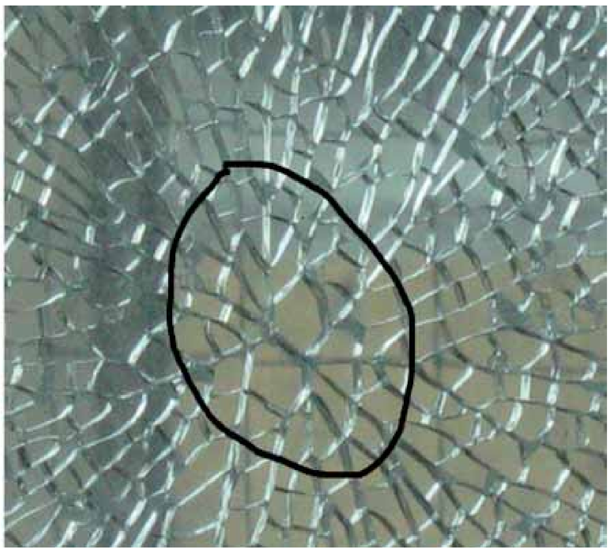
3. Results and discussion

A fractured tempered glass panel from the elevation of selected Cracow building was exposed to visual assessment (Fig. 1a). The fragment of the glass panel with butterfly-shaped fracture network characteristic for the spontaneous fracturing under the influence of NiS (Fig. 1b) was observed by use of an optical microscope. The fragment of impurity was observed by use of SEM analysis (Fig. 2), including the EDAX analysis within micro-areas (Fig. 3). Microscopic examinations proved the presence of about 1 µm inclusions, having oval shape and non-uniform surface (Fig. 2).

Chemical analysis conducted within the micro-area of inclusion proved the presence of considerable amount of nickel and sulphur. Unfortunately, because of small size of the inclusion, there was no possibility to prove the presence of crystalline NiS.

Four batches of glasses 1-4 (Table 1) were melted in order to determine the mechanism of nickel sulphide forming in tempered glass. The raw materials introducing nickel

a)



b)

Fig.1. Fractured tempered glass: a) window panel with fractured glass, b) fracture network.

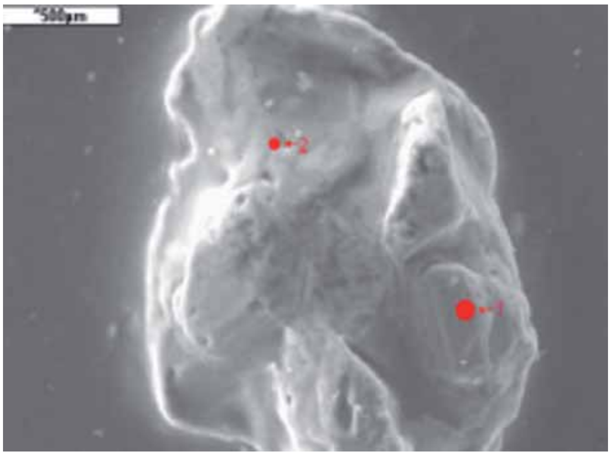


Fig. 2. SEM image of the inclusion in tempered window glass.

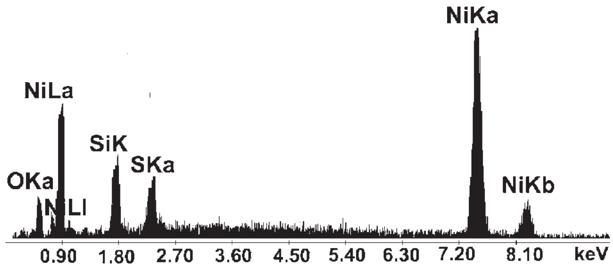


Fig. 3. EDAX analysis of the inclusion formed in tempered glass of the fractured window panel.

(Ni) were used aside from the standard raw materials for the float glass production. Based on the literature data [6], it is assumed that, during melting the batches of the mentioned raw materials, stable in the reductive atmosphere Ni_3S_2 is formed, which reacts with sodium sulphate, resulting in the formation of NiS according to the following reaction:

$$Ni_3S_2 + Na_2SO_4 + 1½C \rightarrow 3NiS + Na_2O + 1½O_2 \qquad (1)$$

No presence of any inclusions was proved in the glasses 1-3 after melting (Table 1), what indicated that the reaction (1) did not run. Transferring the problem onto the industrial scale of glass melting it seems weakly possible from the thermodynamic point of view that Ni_3S_2 was developed in the glass mass, including its bonding with sodium sulphate, which was not decomposed. In case of the glass 4, in which the greatest amount of nickel file dust was introduced, the presence of the inclusions was observed. Fragments of the glass 4, containing the inclusions, were exposed to microscopic examinations and EDAX analysis. The presence of numerous inclusions smaller than 0.5 µm, and individual inclusions bigger than 1 µm, was proved (Fig. 4). The executed EDAX analysis proved in point 1 (Fig. 5) the presence of Cu, Fe and Zn inclusions, which comprise the impurities derived from steel sheets, on which the glass was poured out. Based on the EDAX analysis conducted in point 2 on one of the smallest inclusions, the presence of trace amounts of S, Ni, Cu and Zn was proved.

On the basis of executed XRD and microscope SEM/EDAX examinations aimed at the glass „sandwiches" with nickel sulphide entrapped between two ram material panels it has been proved that keeping reductive conditions in the

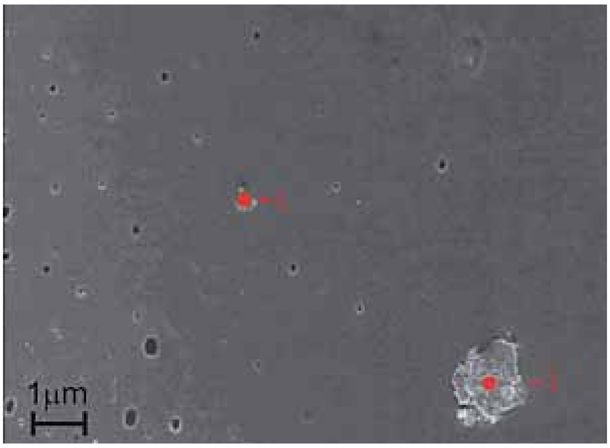


Fig. 4. SEM image of the inclusion derived from a fragment of melted glass 4.

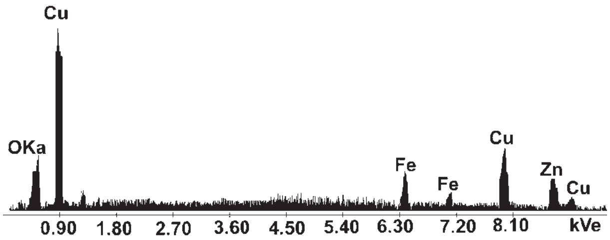


Fig. 5. EDAX analysis of the inclusion derived from melted glass 4 in point 1.

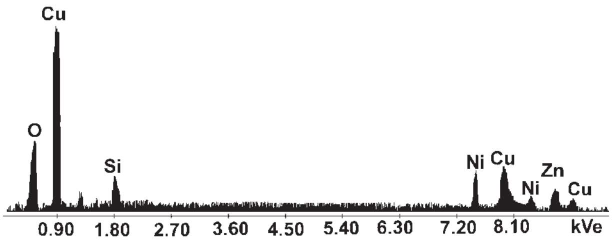


Fig. 6. EDAX analysis of the inclusion derived from melted glass 4 in point 2.

furnace allows NiS preservation in the glass (Figs. 7-10). Moreover, it has been observed, that during tempering of the prepared three glass panels, one of the panels cracked in the heating furnace zone, second one after several hours, and the third one after 3 days of conducting experiment. Observation of characteristic fracture network of the glass panel, which was broken after 10 days without the external factor intervention proves the existence of α-NiS inclusions in the glass.

In order to reduce the inclusion size, the experiment comprising the placing nickel sulphide and zinc sulphate between two glass panels has been conducted. The resultant "sandwiches" were melted in the furnace at the temperature of 1050°C. After annealing, three flat 6 mm thick glass samples with the visible inclusions were obtained. The XRD and SEM/EDAX examinations of the developed inclusion proved the presence of crystalline phase of nickel oxide NiO (Figs. 11-14). Zinc sulphate played the role of oxidizer during the glass melting. Sulphur from NiS was oxidized and transformed into sulphate. The temperature of $ZnSO_4$ decomposition (740°C) is much less than in the case of Na_2SO_4. That is why thermal decomposition will take place only after absorption

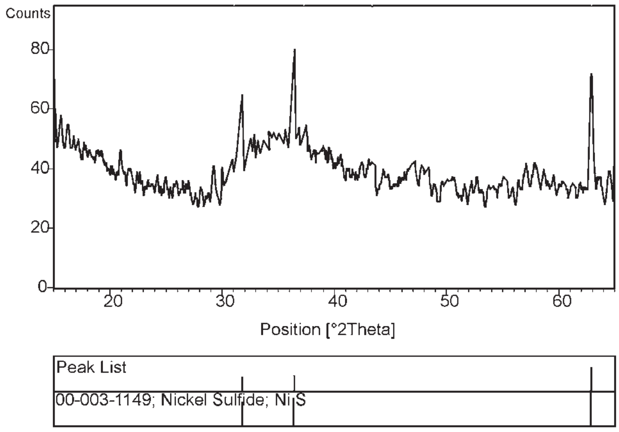


Fig. 7. Diffraction pattern of the NiS inclusion entrapped between two glass panels.

Fig. 8. Optical image of NiS inclusion entrapped between two glass panels.

Fig. 9. SEM image of the NiS inclusion entrapped between two glass panels.

of sulphur derived from lower-temperature decomposition of zinc sulphate. This caused complete decomposition of nickel sulphide accompanied by the presence of increased amount of sulphur.

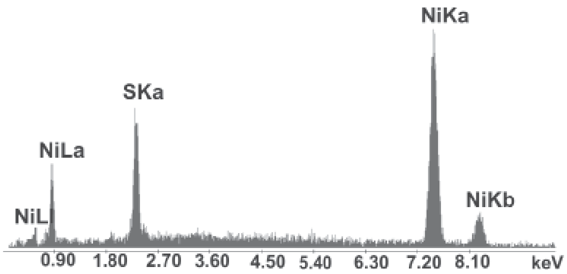


Fig. 10. EDAX analysis in point 1.

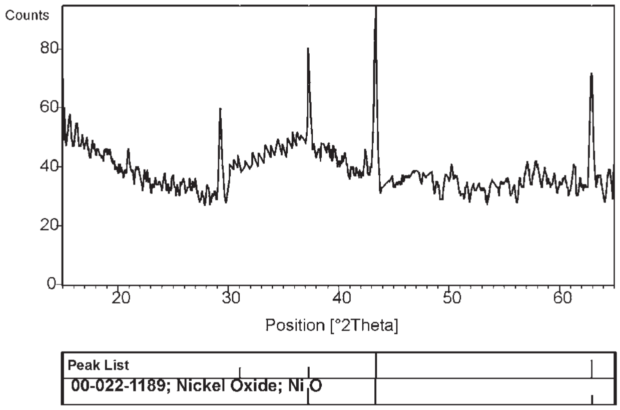


Fig. 11. Diffraction pattern of the NiO inclusion entrapped between two glass panels.

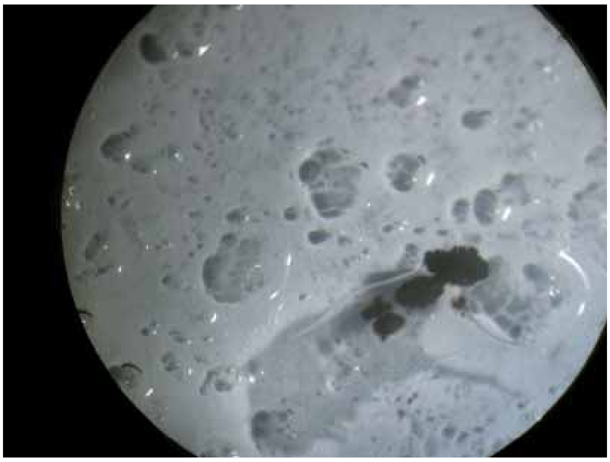


Fig. 12. NiO inclusion entrapped between two glass panels.

4. Summary

The executed analysis of fracture network of a tempered glass panel, which was spontaneously broken without mechanical factor intervention, and the microscope and chemical composition EDAX analysis within the inclusion zone proved that the inclusion is built of nickel sulphide. Initiated fracturing in the tested glass panel is derived from the characteristic butterfly-shaped area, in which nickel sulphide inclusions were found. The glass chemical compositions, in which nickel-bearing raw materials were used, have been designed in order to recognize the mechanism of inclusion formation. The examinations were aimed at stimulation of the nickel sulphide development in melted glasses. No inclusions were proved in melted glasses obtained with the

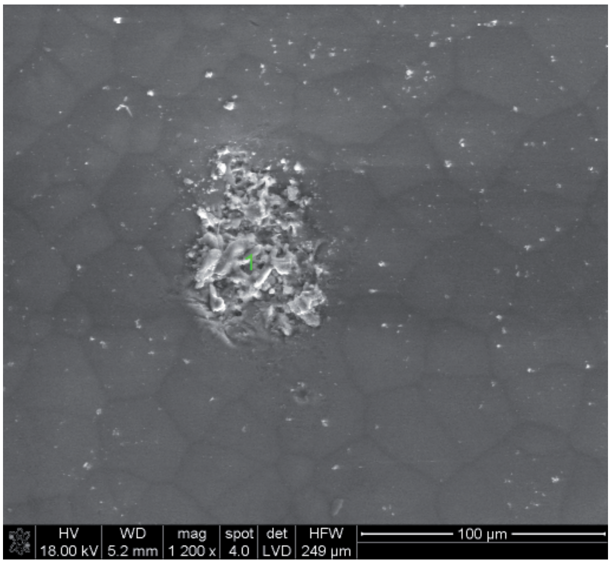


Fig. 13. SEM image of the NiO inclusion entrapped between two glass panels.

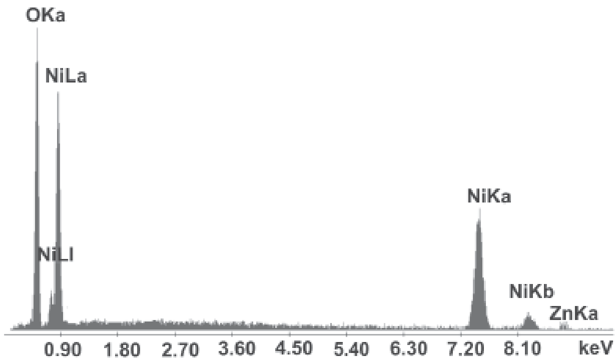


Fig. 14. EDS analysis in point 1.

additives of metallic nickel, or nickel file dust and sulphur. The glass added with the increased amount of metallic nickel was tinted in brown-gray colour, and metallic nickel played the dye role in this case. Inclusions were found in the glass composed of standard raw materials and added with metallic nickel, nickel file dust and sulphur. The executed microscope analysis and EDAX analysis of the glass fragment with inclusions allowed proving that the inclusion contains sulphur and nickel. Both XRD and microscope SEM/EDAX examinations of the inclusions, developed as a result of entrapping nickel sulphide, proved the presence of NiS. When zinc sulphate and nickel sulphide were introduced between glass panels, the presence of NiO phase was proved. NiS can be derived from loaders or burners made of nickel alloys containing impurities of sulphur or nickel sulphide.

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