Adapted Heat Treatment for Phase Transformation of NiS Inclusion in the Heat Strengthened and Tempered Glass

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2 = Nickel sulfide
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Abstract

To avoid spontaneous breakage of heat-strengthened and tempered glass is one of most important subjects of glass products in buildings and automobiles. Several attempts have been so far made for empirical basis of heat treatment or phase transformation of NiS by many authors. However, we found few investigations into the nucleation frequency of the phase transformation of NiS inclusions, although there are many studies of the rate of transformation with respect to the holding temperature and time.

Effective frequencies of nucleation and crystal growth of NiS inclusion depend on the rate of the temperature increase in the heat soak process of tempered and heat-strengthened glass. They also depend on the composition of crystalline NiS (the compositional ratio of Ni and S and additional elements such as Se and Fe in NiS). Maintaining the temperature and time of NiS at the maximum temperature affects the growth rates of transformation from the alpha to beta phases of crystalline NiS. New technical methods, i.e. the heat treatments necessary to transform from the alpha to beta phases of NiS, are described in this paper.

Introduction

Heat-soak treatment serves to prevent spontaneous breakage of heat- strengthened and tempered glasses in many glass-making companies (1)(2). Spontaneous failure of the glass is caused by volumetric expanding of the phase transformation (from the alpha, in a high-temperature form, to beta phases in the low temperature form) of nickel sulfide (NiS) with different compositional ratios of Ni and S (1)(2)(3)(4). The formation of crystalline NiS in the soda-lime-silicate glass (so called float glass) has been explained by the reaction between metal and alloy particles with the Ni components and molten glass, or chemical absorption of the Ni components, including burner flame, during the glass-making process.

It is very difficult to reduce the NiS stones in the glass-making process; therefore, the heat-soak treatment of glass products is employed to exclude the NiS defects. The nickel sulfide in the glass is composed of several crystalline phases of NiS with different chemical compositions. The transitional temperatures from the alpha to beta phases can be changed by varying amount of sulfur in the NiS. Different kinetic parameters have been found for different compositions of NiS (1)(2)(3).

Researchers have previously explained that the phase transformation of NiS is strongly dependent on the holding temperature and time at the maximum temperature during the heat soak test. We have investigated phase transformations of crystalline NiS with different compositions of Ni and S in glass products for several years, and suggested a reliable heat-soak process to make high-quality, heat-strengthened and tempered glass. In this paper, the kinetics of the phase transformations of NiS and a new technology of heat-soak treatments are provided, based on several experimental results.

Experimental procedure

We studied the phase transformations of NiS in glass using a polarizing optical microscope attached to thermocouples on the glass surfaces, which were controlled from 25°C (room temperature) to 500°C. NiS particles of several grain

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sizes in the glass were collected from the defects in the float glass products. Measurements were repeatedly performed under differing rates of increasing and decreasing temperatures while the time at the maximum temperature was maintained. We used more than twenty glass samples in the experiments.

The transformations of NiS from the alpha to beta phases were confirmed, on the basis of the intensities of the interference colors, which were formed by the compressive stress around the particle, under crossed-nicol conditions with a 530 nm sensitive color plate (compensator) at a diagonal position. The heat-soak treatment procedure which we adapted, was determined using the results of the experiments, and the performance of the NiS heat-soak process was established by comparison with several productive processes.

Results

Phase transformations of NiS

NiS particle in the glass showed spherical or sometimes ellipsoidal forms (Fig.1). They were composed of several crystalline phases of nickel sulfides, i.e. Ni_3S_2, Ni_7S_6, NiS, NiS1.01, and Ni_2S_3. The crystalline form of the NiS can be detected by the analytical data of micro X-ray camera patterns. The transitional temperatures of each NiS phase differed among the different associations of the crystalline phases. Therefore, the rates of the phase transformations from the alpha to beta phases of NiS in glass are dependent on the amounts of Ni_7S_6, NiS, and NiS1.01 in the particle (see Table 1).

Figure 1. NiS particle after spontaneous failure of tempered glass.

We can confirm the transformation of the NiS by the intensity of the interference colors under a thermally controlled microscope. The maximum degree of interference color and growth of micro cracks around the NiS particle indicate the beta phase of NiS (Fig.2).

Table 1. Comparison of temperature of phase transformations of NiS.

crystalline NiS	phase assemblage	transitional temp.
Ni7S6	Ni3S2 + Ni7S6	397
	Ni7S6	400
	Ni7S6 + NiS	400
NiS	Ni7S6 + NiS	379
	NiS	379
NiS1.01	NiS1.01 + Ni3S4	282-356

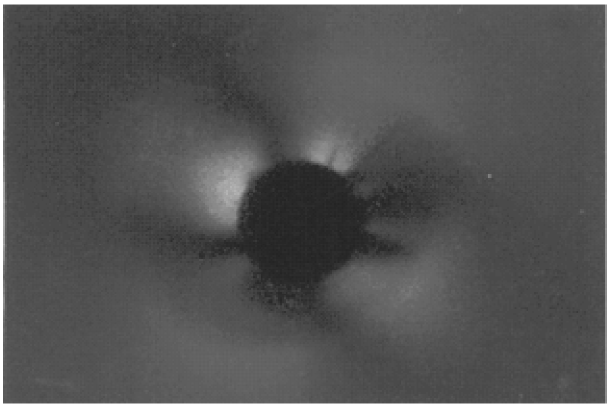

Figure 2. Perfectly transformed beta phase of NiS in the glass after heat soak treatment.

Figure 3 shows time-temperature-transformation (T-T-T) diagrams, which clarify the reversible transformation from alpha to beta phases of the crystalline NiS particle in the glass. The beta NiS start to nucleate at 140°C (the open circle shows incomplete state of the interference color), at a low rate of increasing temperature (about 10°C/min). The stable temperature of the beta phase of the NiS ranges from 200°C to 300°C under the same conditions (temperature and time).

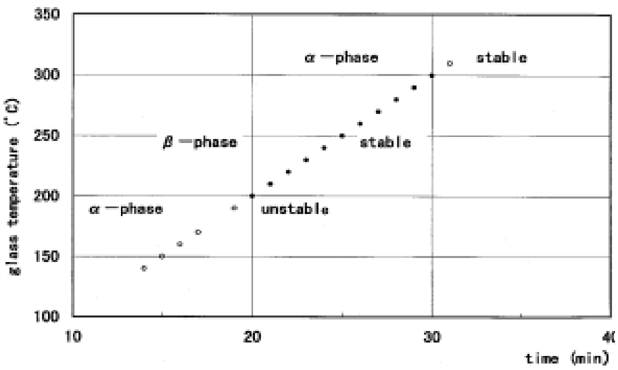

Figure 3. Time-temperature-transformation (T-T-T) diagram of crystalline NiS.

Figure 4 shows the T-T-T diagram from the alpha to beta transformations of the NiS in the glass. The stable area of the beta-phase differs due to the different rate of rising temperature in the heat-soak treatment. The temperature of nucleation and crystal growth of the beta NiS at a low rate of increasing temperature is lower than that at a high rate of temperature increase. The stable area of the temperature of the beta NiS is wider under the lower rate of temperature increase. The stable area (temperature and time) of the beta phase of the NiS is wide; therefore, we can perform heat treatment of the NiS at a lower temperature (from 200°C to 250°C) at a low rate of temperature increase (less than 10°C/min).

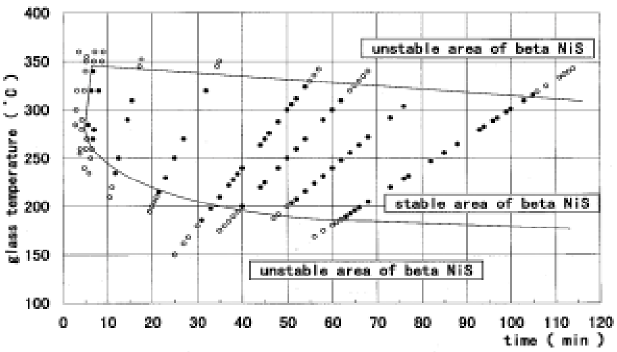

Figure 4. T-T-T diagram of NiS at the different rate of rising temperature.

The NiS defects which contain other elements such as selenium (Se) and iron (Fe) in the colored-glass (brownish or greenish colored glass) , can transform from the alpha to beta phases at a lower rate of temperature increase (less than 10°C/min).

Low cost heat soak treatment

The heat soak treatment of NiS is expensive in terms of personnel, electric power and equipment costs. We must reduce these costs in the newly adapted heat treatment technique.

Figure 5 shows the schematic diagrams of the new heat-soak treatment technique that maintains the temperature from 150°C to 300°C immediately after quenching process of heat-strengthened or tempered glass. The stable alpha phase of NiS continuously transforms to stable beta crystals in the glass, so that the defects can be removed by

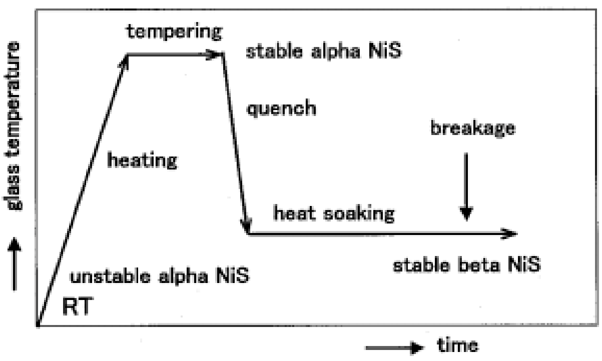

Figure 5. Schematic diagrams of new heat soak treatment.

spontaneous breakage. We can automatically perform the heat-soak process, and effectively reducing production costs.

Conclusions

Our investigations of the phase transformation from the alpha to beta phases of crystalline NiS and reduction of NiS defects have been conducted for several years. The results obtained regarding NiS defects are as follows.

1) The rates of phase transformations from the alpha to beta phases of NiS in glass depend on the amounts of crystalline Ni_7S_6, NiS, and NiS1.01. They also strongly depend on the heating rate of the glass products.
2) The conditions of the heat-soak treatment (the rate of temperature increase and the holding time at the maximum temperature) can be determined in time-temperature-transformation (T-T-T) diagrams, which have been determined by the experimental procedure.
3) We can realize low cost heat-soak treatment using the new technique, which maintains a constant temperature immediately after the quenching of tempered glass. We can achieve shortening of heat treatment of the NiS and cost down of the operating.

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