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Refining of glassy materials with aluminium compounds nano-molecules

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A new technology of refining soda-calcium-silicon glassy surfaces with aluminium compounds nano-molecules has been shown in the present study. A structural definition of aluminium compounds nano-powders exposed to thermal processing, including grain-size analysis, has been discussed. Optimal technical and technological parameters of the refining process have been selected. The method of refining soda-calcium-silicon glassy surfaces with aluminium compounds nano-molecules ensures profitable operational properties of the glass, such as increased bending strength, scratching resistance, micro-hardness and chemical resistance without deterioration of the optical properties. Nano-molecules were spread onto the heated glass surface, or onto the cold glass surface and then heated up to temperatures close to the glass transformation, when nano-molecules penetrate into the glass surface. Testing results of the glass operational properties, such as bending strength, scratching resistance, micro-hardness, chemical resistance and optical properties have been presented. The received results develop new possibilities with respect to opaque glass, float glass and glass fibres, as well as to glass processing.

Keywords: glass, nano-molecules, aluminium powder, refining.

1. Introduction

Glass is a kind of material having relatively high compressive strength but very low tensile, bending and striking strength. Insufficient mechanical resistance of glass and its brittleness restrict a broad use of the glass employed as construction material. That is why numerous trials of improving the glass resistance have been made. The glass resistance depends first of all on the condition of its surface, and secondary on its chemical composition, annealing degree, uniformity, environment and temperature. The presence of glass surface defects resulted in the development of numerous methods aimed at the improvement of glass strength which could eliminate micro-fractures, protect the glass against secondary defects or expose the glass surface to the action of compressive strengths eliminating such defects [1].

Modification of the glass surface with the use of the above mentioned methods considerably improves mechanical strength of the glass. One of the mentioned glass refining methods comprises thermal processing, the so-called glass hardening. The glass is heated up to such temperature that from one side the glass could reach suitable rigidity not being deformed during industrial processes, and from the other side had suitably low viscosity to ensure fast relaxation of the internal strengths. Therefore, after the air cooling, the surface is shrunk and rigid, while its internal zones are fluid. During the cooling process the internal shrinkage of the glass is limited by rigid external layers, what in consequence leads to the fact that after final cooling, compressive strengths compensated by internal tensile forces act on the glass surface. In the final phase of the process, temperature distribution fades and only strength distribution is left. Thermal hardening enables production of glasses of considerably higher mechanical resistance than was observed in case of traditionally annealed glasses.

The improvement of strength properties can also be obtained by chemical etching of the glass in hydrofluoric acid solutions. In the initial phase of the process, etching fluid penetrates into fractures rounding their originally sharp ending, what results in a qualitative change of the defect-making strength concentrator of a lower damage degree. Final resistance depends not only on the thickness of the liquidated layer but also on the quality of the glass surface after etching process, what is related to the composition of the etching liquid, its temperature and mode of the process realisation.

The next method comprises a surface ion exchange. The exchange enables a considerable increase in glass bending strength compared to glass not exposed to such process, and also an increase in impact resistance and hardness. Basing on the available theoretical and practical data, we can suppose that the best results in soda-calcium glass are obtained with the use of melted potassium nitrate KNO_3, under the glass processing temperature being about 100 °C lower than the transformation temperature [2].

The glass surface can also be refined by the „hot" method, where glass of 450–600 °C is exposed to the action of $SnCl_4$, which when contacted with the hot glass surface is chemically decomposed, forming an oxygen film on the glass surface. Moreover, the diffusion of tin oxide into near-surface glass zone takes place. Structural bonding with the glass is formed and considerable changes of the glass surface take place, *i.e.*, glass surface smoothness is increased, thus scratching resistance and glass hardness increase, what results in the improvement of mechanical impact resistance of about 30%. The spread film is resistant to the action of hot water, vapour and lye, including variable atmospheric conditions [3].

The development of nano-technology, being a technology of new generation, is commonly used in various branches. The technology of ultra-thin layers is the best example. Nano-technology also makes use of very fine-grained powders [4, 5].

Nano-powders considerably improve mechanical, thermal, electrical and magnetic properties of ceramic materials and glass, as well as composites. Such material parameters as strength, ductility, brittleness, light transmittance, or dielectric transmittance can be modified by intervention into material microstructure resulting from the change in particle dimension or the addition of nano-powders. The procedure of obtaining nano-particles with the use of milling method is shown in the present study. Aluminium compounds nano-powders have been defined with respect to their structure and grain-size and glass surface type. Glass surface refining experiments have been described [6].

2. Experimental

Aluminium hydroxide has been used as a base substance of the nano-powder, which was mechanically powdered together with enveloping substance in a rotary-vibrating mill. Milling is the most commonly used method in nano-powders making technology. The process comprises the diminution of a base material grain-size. The process is activated by external forces, which generate in grain stresses exceeding their mechanical strength. Milling methods give much more massive product than chemical methods.

Powder prepared in such a way was tested by a DTA/DSC analysis in order to determine the mode of phase transformations which occur when nano-powders of aluminium compounds are heated up. The results were recorded using a DTA-7–Perkin–Elmer thermo-analyser. The measurements were conducted in nitrogen atmosphere. 60 mg samples of nano-powder were heated up in platinum crucibles with a constant heating rate of 10 °C/min^{-1}, from room temperature up to 1450 °C. In order to determine crystalline phases, thermally processed nano-powders and base nano-powder were tested using RTG analysis. Tests have been executed with the use of a X'Pert Philips Pananalitical diffractiometer.

An electron microscope and Nanosizer-ZS – Malvern Instruments were used in order to define the grain-size, what allowed to determine basic parameters describing suspended particles, *i.e*. grain-size of particles ranging from 0.6 nm to about 6 μm. The measurement of the particle grain-size was based on Brovian movement phenomenon and dynamic light scattering (DLS). The measurement was made in water, and the use of an ultrasonic disintegrator allowed more effective disintegration of agglomerates and measurement of real particle grain-size.

Nano-powder prepared in such a way was then spread on the glass surface of the hot sections of previously formed glass products (opaque glass, light bulbs). The nano-powders can also be spread in the production of float glass by a float method, during glass rolling, glass pipe drawing, glass fibre production and glass processing. In this case, nano-molecules of aluminium compounds are spread onto a cold glass surface and then heated up to temperatures close to glass transformation temperature. After such spreading, the process of diffusion of nano-molecules on the glass surface takes place within the phase of the formed glass product annealing (opaque glass, light bulbs, float glass, glass fibres and processed glass).

The measurement of transmission within ultraviolet light (UV) and visible light (VIS) was made on glass samples with a nano-powder film, with the use of a Hawlett Packard 8453 spectrophotometer, equipped with a deuterium discharge lamp (UV) and a wolfram lamp (VIS).

Transverse bending strength and micro-hardness tests have also been executed. The measurement of transverse bending strength was made using a standard instrument of 50 mm spacing and a loading rate of 30 mm/min. Micro-hardness tests were made by Vickers method with the use of a PMT – 3 micro-hardness-meter, under various loads of a diamond head (300–500 mN).

Hydrolytic resistance of the glass surface with a nano-powder film of aluminium compound, according to Polish standard PN-ISO 4802-1, was also tested. The samples were exposed to water action for a period of 60 minutes, in water temperature of 121 °C. Resistance was determined by titration of the amount of alkalis in extraction solution, using hydrochloric acid 0.01 mol/l.

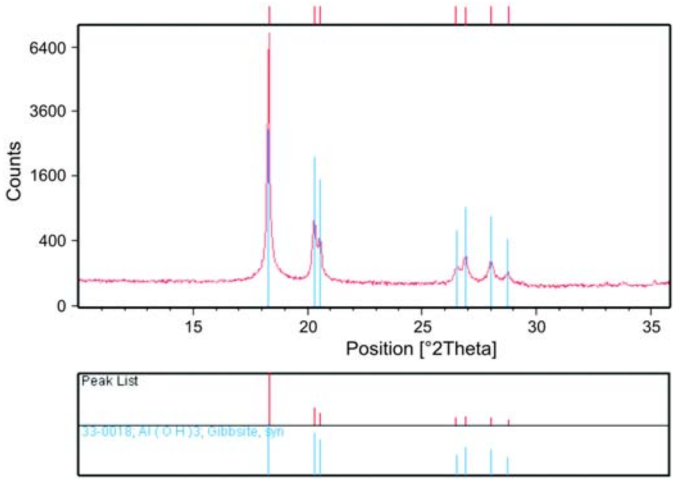

Fig. 1. Roentgenogram of aluminium compounds nano-powder.

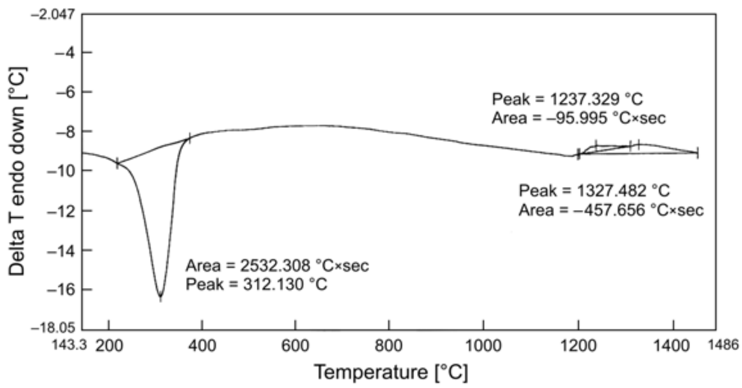

Fig. 2. Thermal analysis by DTA of aluminium compounds nano-powder.

3. Results and discussion

RTG examinations of mechanically disintegrated aluminium hydroxide proved the occurrence of a gibbsite phase of $Al(OH)_3$, what is shown in Fig. 1.

Thermal analysis by DTA has been made in order to determine phase transformations occurring during heating up of aluminium compounds nano-powder. The measurements by DTA (Fig. 2) allowed to prove the occurrence of two thermal effects. An endothermic effect occurring at 312 °C and an exothermic effect commenced at 1240 °C.

After obtaining the results of the thermal analysis, the powder was exposed to thermal processing in a temperature range of endothermic and exothermic effects. Nano-powder soaking was conducted within a temperature range of 320 °C and 1240 °C. The RTG examinations proved the presence of diaspore AlO(OH) at 320 °C, whereas at the temperature of an exothermic effect the presence of corundum (α-Al_2O_3) was proved. Results of RTG examinations are shown in Fig. 3.

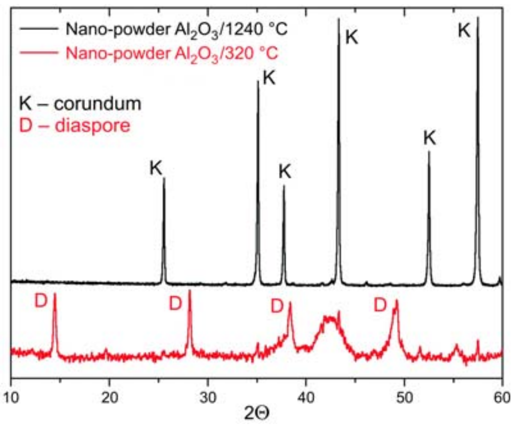

Fig. 3. Roentgenogram of aluminium compounds powder soaked at 320 °C and 1240 °C for 1 h.

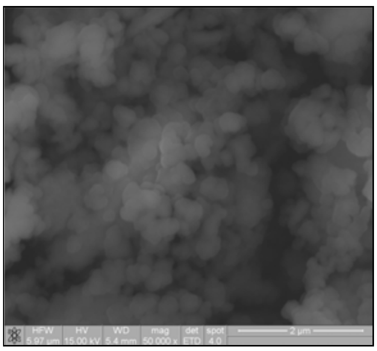

Fig. 4. Nano-powder of aluminium compounds – SEM photo.

Aluminium compounds nano-powder grain-size was determined using an electron microscope, as well as by a sieve analysis. The results of an electron microscope analysis are shown in Fig. 4.

A grain-size analysis made with the use of Nanosizer-ZS – Malvern Instruments allows to determine the volume and numerical fraction of particles. Results of grain-size analysis are shown in Figs. 5 and 6.

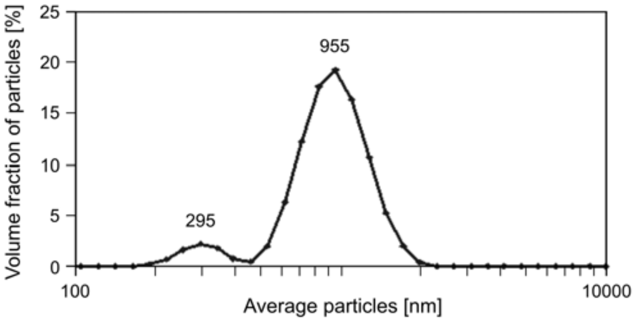

Fig. 5. Volume fraction of particles.

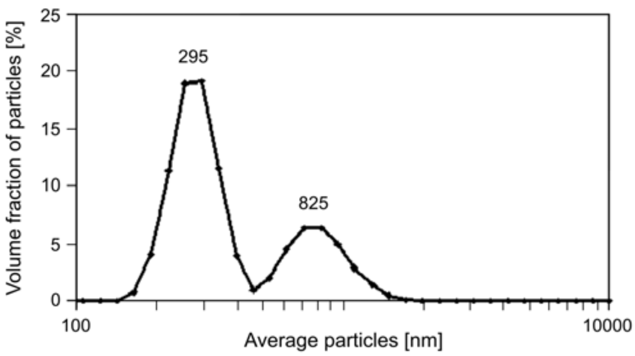

Fig. 6. Numerical fraction of particles.

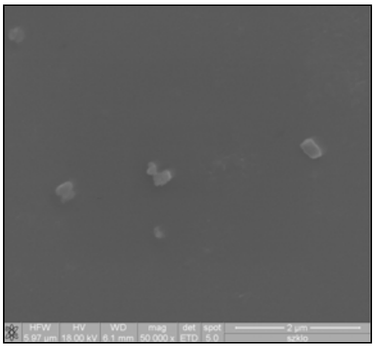

Fig. 7. Base glass surface – SEM photo.

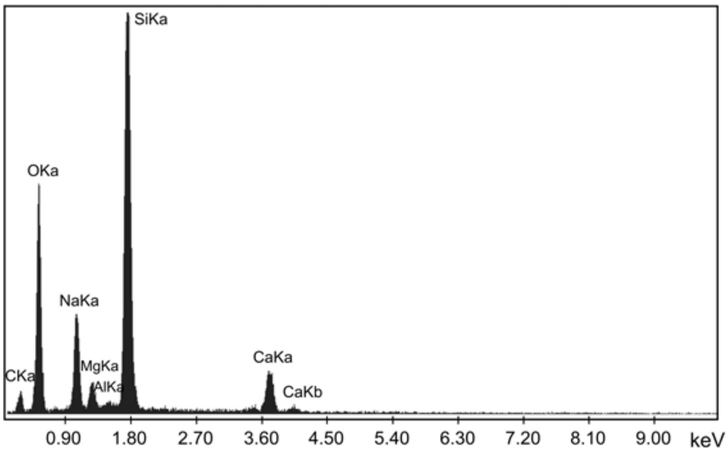

Fig. 8. EDAX analysis of the base glass surface.

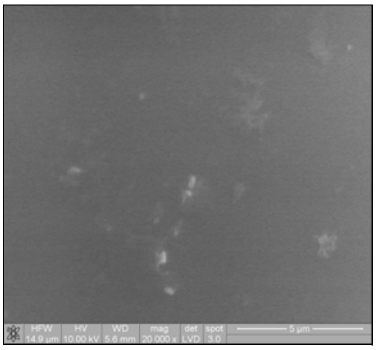

Fig. 9. SEM photo of the glass surface after refining with aluminium compounds nano-molecules.

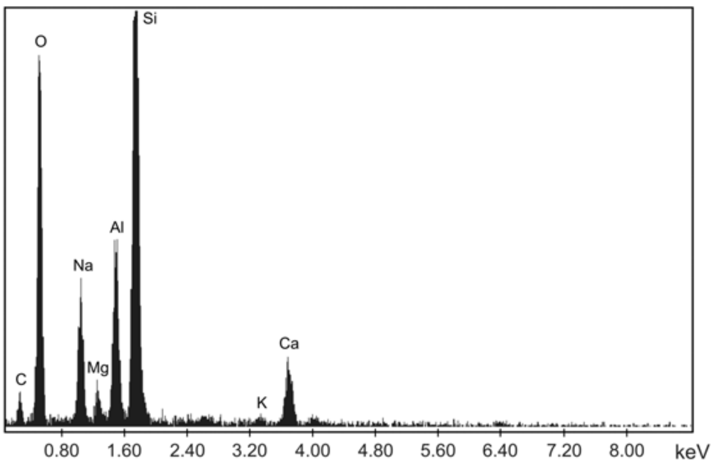

Fig. 10. EDAX analysis of the glass surface after refining with aluminium compounds nano-molecules.

When the grain-size was determined and the phases occurring during heating were defined, aluminium compounds nano-powder was spread onto a glass surface. As a result of spreading aluminium compounds nano-molecules onto the glass surface and as a result of glass processing within a transformation temperature range, the modification of the glass surface structure by aluminium ions takes place. The modification of the glass surface and the results of the layer composition tests are illustrated by SEM photos and the EDAX analysis of base glass, as well as the glass covered with aluminium compounds nano-powder film (see Figs. 7–10).

According to the results of the examination of the modified glass surface, the surface shows improved hydrolytic durability (the Table). Samples with aluminium compounds nano-powder film show improved hydrolytic class ranging from HC3 (samples P1–P3) to HC2 (samples N1–N3).

The samples also proved a considerable improvement in transverse bending mechanical properties and micro-hardness. The examinations were made for various glass types and their results are shown in Figs. 11 and 12.

Samples tested for transverse bending strength showed a considerable increase in strength, even by 46% in case of industrial glass. Micro-hardness tests were made for samples spread with aluminium compounds nano-molecules in temperatures close to the transformation temperature (hot spreading) and at room temperature (cold spreading). Samples spread at room temperature were heated up to temperatures close

T a b l e. Hydrolytic resistance of the glass surface covered with aluminium compounds film.

	Sample					
	P1	P2	P3	N1	N2	N3
Volume fraction of the saline acid solution used to titration [ml/100ml]	3.8	3.5	3.2	1.0	1.2	0.8
Average volume fraction of the saline acid solution [ml/100ml]	3.5	3.5	3.5	1.0	1.0	1.0
Class of hydrolytic resistance	HC3	HC3	HC3	HC2	HC2	HC2
Quantity of oxide of sodium [μg]	1085	1085	1085	310	310	310

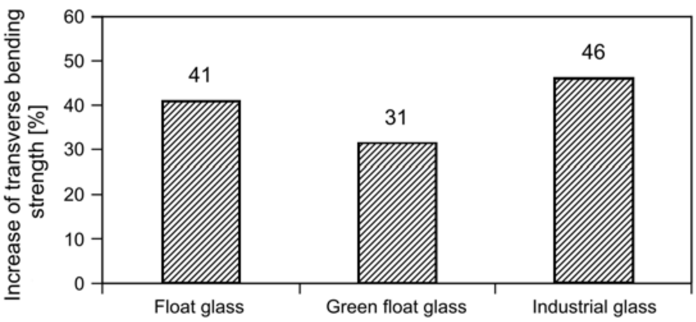

Fig. 11. An increase in transverse bending strength of float glass and industrial glass covered with a film of aluminium compounds nano-powder.

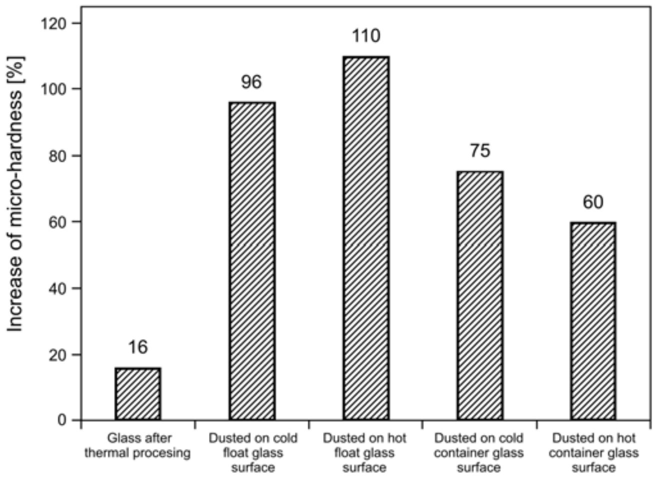

Fig. 12. An increase in micro-hardness of float glass and opaque glass covered with a film of aluminium compounds nano-powder.

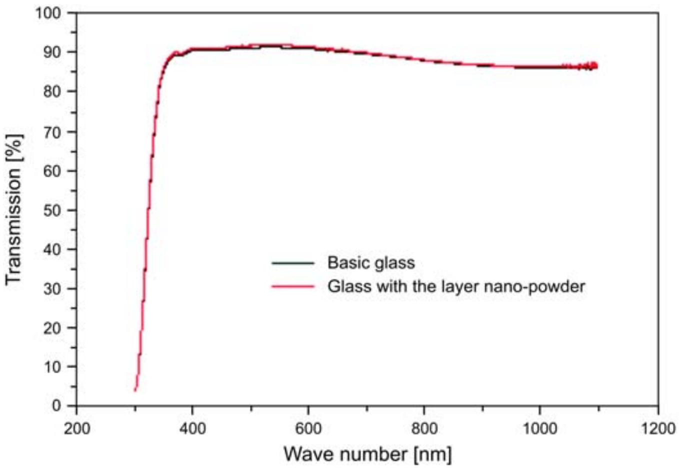

Fig. 13. Light transmittance of the float-type glass.

to the transformation temperature. After such spreading, samples show a relatively high increase in glass surface hardness. The best results were obtained for hot spread float glass samples, which showed a micro-hardness increment of about 110%.

Basing on the results of examinations, including visual observation, the samples did not show any deterioration of optical effects, what is illustrated in Fig. 13.

4. Conclusions

Basing on the results of executed examinations, we can state that the presented method of glass surface refining considerably improves the condition of the glass surface.

Results of DTA and RTG analysis indicate that nano-molecules α-Al_2O_3 can penetrate into the glass surface within a range of transformation temperatures. The presented method undoubtedly develops new possibilities not only in case of opaque glass, float glass and glass fibres but also in the field of glass processing.

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