DEPISTAREA MODIFICĂRILOR STRUCTURALE ÎN STICLELE INCOLORE INDUSTRIALE, EXPUSE ACŢIUNII CÂMPULUI MAGNETIC ÎN IMPULS, PRIN METODA SECȚIONĂRII CU HF ▲

REVEALING STRUCTURAL CHANGES IN INDUSTRIAL COLORLESS GLASSES, EXPOSED TO IMPULSE MAGNETIC FIELD, USING SECTION ETCHING BY HF SOLUTION

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The article presents the results of the investigation which studied the influence of impulse magnetic fields on structural changes in industrial colorless glasses with the help of section etching. Regimes of treatment include: temperature – between 300 and 600 ^{0}C, vector's magnitude of the magnetic induction - up to 0.15 T, duration – between 1 and 600 s. Analysis of structural changes in glasses is made with the help of section etching of solution HF. During one etching a layer of 0.05-10 µm is dissolved. Concentrations of Na^+, K^+, Ca^+ is determined in extracts after etching. Compactness of flat glass structure changes after thermomagnetic treatment. A 5-15 % decrease of dissolution rate of glass surface layers shows it. It is complicated to interprete the results obtained because of the stratified structure of glass. The tickness of the separate layers makes small parts of µm. Analysis of changes in the compactness of glass structure is made depending on the type of magnetic field and its parameters, temperature and duration of treatment magnetic.

În lucrare sunt prezentate rezultatele cercetărilor pentru determinarea influenței câmpului magnetic în impuls asupra schimbărilor structurale în sticlele industriale incolore cu ajutorul decapării secționate. Regimurile de tratare sunt următoarele: temperatura – de la 300 la 600 ^{0}C, valoarea modulului vectorului inducției magnetice – până la 0,5 T, durata – de la 1 la 600 s. Analiza schimbărilor structurale în sticle a fost efectuată cu ajutorul decapării secționate cu soluție HF. Grosimea stratului dizolvat al sticlei în timpul unei decapări variază de la 0,05 la 10 µm. În extracte după decapare au fost determinate concentrațiile Na^+, K^+ şi Ca^{2+}. După tratare termomagnetică compactitatea structurii sticlei de geam se schimbă, ceea ce este demonstrat de micşorarea vitezei dizolvării straturilor superficiale ale sticlei cu 5-15 %. Interpretarea rezulatatelor obținute este complicată din cauza structurii stratificate a sticlei. Grosimea straturilor separate constituie o parte mică de µm. Schimbările în compactitatea structurii sticlei depind de varietatea şi parametrii câmpului magnetic, temperatura şi durata tratamentului magnetic.

Keywords: *industrial colorless glass, impulse magnetic field, section etching, surface layer, structure, microhardness*

1. Introduction

Interaction of inorganic glasses with electromagnetic fields has been studied since the second half of the past century. Particular attention in the published works has been paid to the mechanism of action of magnetic fields on glasses and change of their mechanical strength and thermostability. Thermomagnetic treatment increases mechanical strength of glass by 20-40 % [1, 2], microhardness and thermostability by 10-15 % [2]. Increment of mechanical properties and thermal stability of glass after the effect of electromagnetic fields is compared to the effect which is achieved by application of dealkalization by acid gases [3]. To control the process of thermomagnetic treatment it is necessary to know the mechanism of interaction of magnetic fields with inorganic glass and its structure.

Different methods of physical and chemical analysis are involved in order to investigate glass surface [4]. The spectroscopy methods of analysis - infra red reflection spectroscopy (IRRS), electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS) and many others [4] showed good results while investigating the surface layer (with the thickness from 10 nm to 1 µm).

The method of section etching by HF solution is very effective in studying the interaction of glass of simple composition with water and its solutions [5, 6]. In this case during one etching a glass layer of approximately 0.5 – 1.0 µm is dissolved. The section etching method is used to reveal changes in the composition and structure of surface layers of industrial glass [7,8].

The aim of the undertaken work was to

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investigate structural changes in the industrial colorless glasses under the influence of impulse magnetic fields with the help of section etching by HF solution.

2. Experimental

Various types of industrial colorless glassware: bottles and jars, assorted glassware, ampoules made from medical glass, illuminating glassware and flat glass samples were the subjects of investigation. The chemical compositions of industrial colorless glasses are given in Table 1

Samples of glass were exposed to impulse magnetic fields. The main regimes of the thermomagnetic treatment of glass were the following: temperature – between 300 and 600 ^{o}C, vector's magnitude of magnetic induction - up to 0.15 T, duration – between 1 and 600 s. Parameters of impulse magnetic field: magnetic field strength – 0.064 MA/м, duration of an impulse – 25 μs, pulses follow at a frequency – between 1 and 10 Hz, magnitude of current – 20 кA.

The procedure of glass treatment in magnetic field is the following. Treatment of samples in the impulse magnetic field was held in inductors of different types. The samples obtained were washed by water and wiped by spirit. Samples of glass at room temperature were introduced into the kiln. Then the temperature was raised to the designed, heating was stopped and treatment by magnetic field was carried out. After treatment samples were cooled to room temperature in the closed kiln.

At the first stage of investigation three samples of glass were fixed in fluorocarbon polymer cassettes and then were joined to the polymer wheel and put into a weak HF solution (0.1 % weight). The samples were rotated in the solution with speed 100 rotations / minute. After etching the samples were washed with distilled water, dried and weighed. Duration of etching changed within 2.5 to 60 minutes. The temperature of the HF solution was (30±0.1) ^{o}C.

Thickness of the dissolved layer and rate of etching were calculated based on mass losses of the sample before and after etching [8].

During one etching a layer of glass with thickness from 0.05 up to 1.0 μm is dissolved. The relative error of the experiment did not exceed ±4 %. Concentrations of Na^{+}, K^{+} and Ca^{2+} were measured in extracts after etching by the method of flame photometry. Attention should be paid to the fact that an error is made while calculating the rate of glass dissolution and thickness of an etched layer. It is connected with inexact determination of density of a surface layer which usually differs from the density of the bulk. Besides this, it is considered that all surface samples are etched with the same rate. In the following experiments samples were kept in solution in stationary position, i. e. without rotation.

The microhardness of samples of glass was meausred. The value of microhardness was measured by the microhardnessmeter PMT-3M. The procedure of microhardness measuring was the following. Each sample was pricked by a diamond pyramid about 20 times. In order to obtain reproducible results the duration of loading on the pyramid was 10 s and duration of exposition of glass surface – 5 s for every measurement. The indentation length was measured twice. The load on the indenter of the diamond pyramid Vickers made 0.5 N. The relative error of determination of microhardness did not exceed ± 4 %.

3. Results and discussions

Preliminary experiments showed that the rate of dissolution of glass depends on the temperature of the HF solution and its concentration, on the volume of solution and on the time of its action on the samples and on hydrodynamics conditions. The temperature of the HF solution, its volume and concentration remained unchanged in all experiments. The dissolution of surface layer with the necessary thickness was achieved at the expense of different time of etching and changes of hydrodynamics conditions (the samples were rotated in the solution or kept in stationary position).

The rate of glass dissolution in HF solution substantially depends on hydrodynamics

Table 1

Chemical compositions of industrial colorless glasses
Compozițiile chimice ale sticlelor industriale incolore

Glass type *Tip de sticlă*	Weight content of oxides, / *Oxizi, partea de masă*, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Other
Flat *Geam*	72.65	1.55	0.11	7.60	3.71	13.62	0.35	0.31	-
Container *Ambalaj incoloră*	71.81	2.55	0.07	6.53	4.63	13.94	-	0.34	-
Medical *Medicinală*	72.81	4.52	0.05	6.05	0.82	8.15	1.64	-	6.11 B_2O_3
Illuminating *Iluminare incoloră*	73.02	1.92	0.04	6.85	-	16.58	1.17	0.29	-
Assorted *Menaj incoloră*	71.47	2.37	0.03	7.59	0.15	17.81	0.38	0.26	-

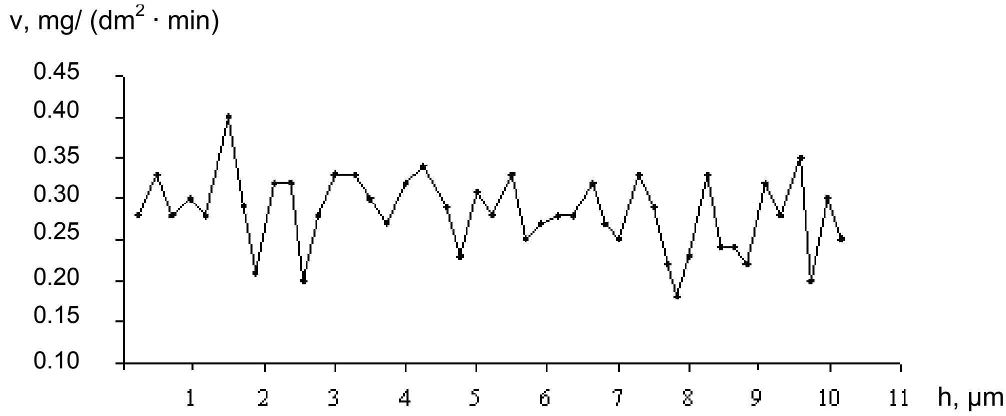

Fig.1- Rate of dissolution of flat glass. The samples were kept in HF solution in stationary position. Duration of one etching -20 minutes. *Viteza dizolvării sticlei de geam. Probele se aflau în soluție HF în poziție staționară. Durata unei decapări - 20 minute*.

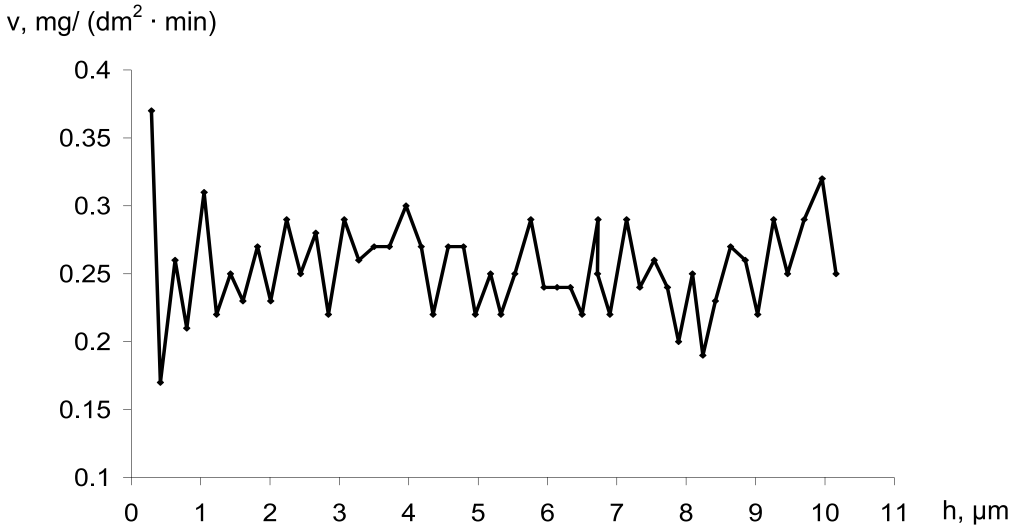

Fig.2 - Rate of dissolution of container colorless glass. The samples were kept in HF solution in stationary position. Duration of one etching -20 minutes. / *Viteza dizolvării sticlei de ambalaj incoloră. Probele se aflau în soluție HF în poziție staționară. Durata unei decapări - 20 minute*.

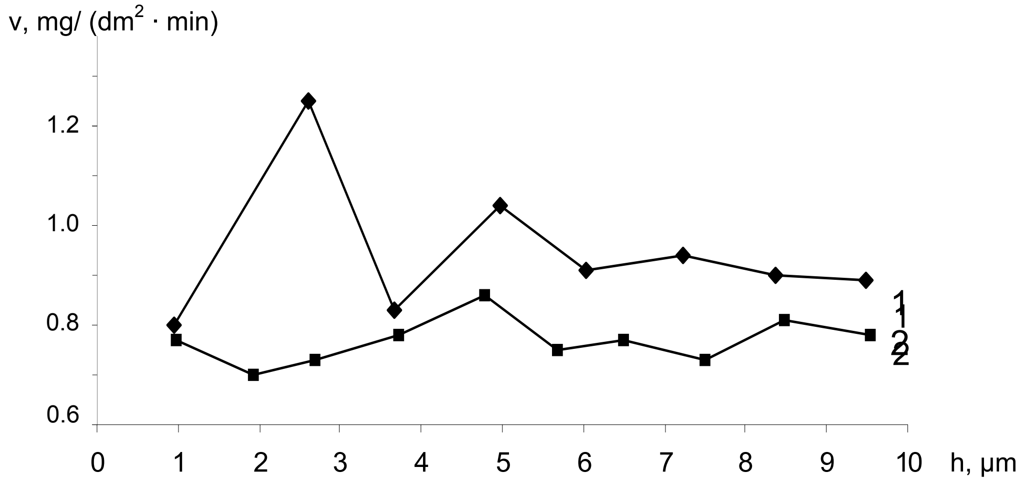

Fig.3 - Rate of dissolution of flat glass. The samples were rotated in the HF solution. Duration of one etching -10 minutes. *Viteza dizolvării sticlei de geam. Probele au fost rotite în soluție HF. Durata unei decapări - 10 minute*.

conditions. For example, Figure 1 and Figure 2 show the graphics of dissolving rate of flat and container colorless glasses, the etching time is 20 min (during the etching samples were in stationary position).

Figure 1 and Figure 2 show that a layer of glass with a thickness of about 0.20-0.25 μm is dissolved during one etching. Attention should be paid to the instability of the dissolution rate. The smallest value of the rate of dissolution is twice as big as the greatest value.

When reducing the duration of one etching from 20 to 10 minutes, the average rate of dissolution of glass remains at the same level, while the thickness of dissolved layer of glass etching is twice reduced.

Rotation of samples leads to a substantial increase in the rate of glass dissolution, as evidenced by the data in Figure 3.

The given facts prove that the dissolving rate of flat glass samples of one and the same series is not stable. It is important that the dissolving rate of the samples of different series differ very much among them. Repeated many times, the etching of flat glass samples of different series did not let us get the reproducible results for dissolving rate. Data comparison of Figure 1, Figure 2 and Figure 3 gives the ground to make a conclusion about stratified structure of industrial glasses. In order to identify heterogeneity of alkali-silicate glasses at the nano- and sub-nanometric level other investigation methods have to be used, example [9,10] More than this with the help of section etching it is possible to estimate the thickness of separate layers.

The rate of glass dissolution in HF solution becomes more unstable when the samples are in stationary position.

We failed to establish a clear correlation between the rate of dissolution and the concentration in surface layers of flat glass Na^+, K^+, Ca^{2+}. Clear longitudinal strips of different width were revealed with the help of light microscopy. Thickness of the separate layers makes small parts of μm.

The rate of dissolution in HF solution of all the industrial glasses (without thermomagnetic treatment) is not stable. The experiments showed that the illuminating and assorted glassware, ampoules made from medical glass, bottles and jars consist of layers without any determined orientation.

The influence of impulse magnetic fields on the rate of flat glass dissolution is shown in Figure 4.

The structure of glass surface layers becomes more compact being treated by impulse magnetic fields. The rate of flat glass dissolution after thermomagnetic treatment decreases by 5–15 %.

In Figure 4 the rates of flat glass dissolution, subjected to the influence of constant and impulse magnetic fields are compared. As it is seen, the impulse magnetic field changes the glass structure to a greater extend than the constant magnetic field.

It was also established that thermomagnetic treatment increases the microhardness of flat glass by 10–15 %. Thus, the glass structure under the electromagnetic influence becomes more compact. A correlation between the microhardness of treated glass and the rate of its dissolution has been established. The higher is the glass microhardness, the lower is its rate of dissolution in HF solution.

Generally, the higher is the value of vector's magnitude of magnetic induction, treatment temperature and its duration, the more compact becomes the glass structure.

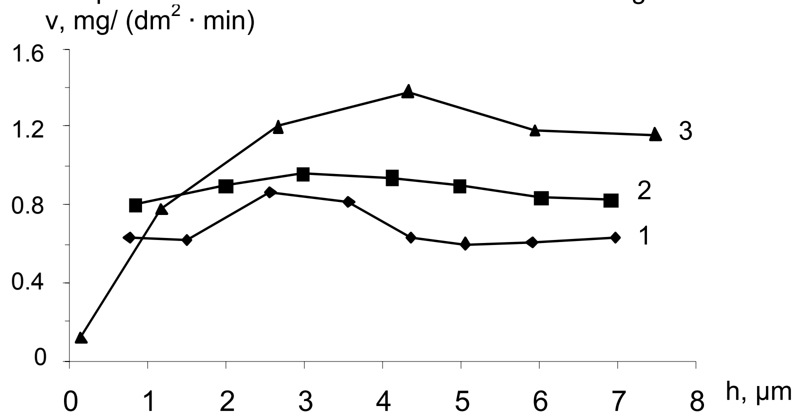

Fig. 4 - Rate of dissolution of flat glass, treated by electromagnetic fields. The samples rotated in the HF solution. Duration of one etching – 10 minutes./ *Viteza dizolvării sticlei de geam, tratată cu câmpuri electromagnetice. Probele au fost rotite în soluție HF. Durata unei decapări - 10 minute*.

1, 2 – treatment of impulse magnetic field: / *tratarea cu câmpul magnetic în impuls*
- vector's magnitude of the magnetic induction - 150 mT; / *modulul vectorului inducției magnetice - 150 mT;*
- temperature – 550 ^{0}C; / temperatura – 550 ^{0}C;
- number of impulses during the sample treatment – 30 (1) and 100 (2); / *numărul impulsurilor de prelucrare a probei* – 30 (1) şi 100 (2);
- pulses follow at a frequency – 0.8 (1) and 1.6 (2) Hz; / *frecvența de repetare a impulsurilor* – 0.8 (1) şi 1.6 (2) Hz;

3 - treatment of constant magnetic field: / *tratarea cu câmpul magnetic constant*:
- vector's magnitude of the magnetic induction - 150 mT; / *modulul vectorului inducției magnetice - 150 mT*;
- temperature – 550 ^{0}C; / *temperatura* – 550 ^{0}C;
- duration – 30 s. / *durata* – 30 s.

4. Conclusion

The rate of dissolutoin of industrial colorless glasses surface layers in HF solution is not stable.

The structure of industrial colorless glasses becomes more compact being treated by impulse magnetic fields. The rate of flat glass dissolution after thermomagnetic treatment is decreased by 5–15 %.

A correlation between the microhardness of treated glass and the rate of its dissolution has been established.

REFERENCES

1. A. G. Andonov, Strengthening of glass bottles by pulsed magnetic fields, Glass and Ceramic, 1998, **55** (7-8), 208.
2. V. A. Sharagov, M. S. Lyubarskii, Effect of a constant magnetic field on the mechanical properties of container glass, Glass and Ceramic, 1994, **51**(3-4), 120.
3. V. Sharagov, Gh. Duca, Increasing physical and chemical properties of annealed hollow glassware as well as of those stored and used, Romanian Journal of Materials, 2013, **43** (1), 68.
4. V. Rupertus, K. Bange, Sophisticated techniques for studying glass surfaces, Extended Abstracts of the International Congress on Glass, 2001, Vol. 1, p. 83.
5. Z. Boksay, G. Bouguet, Fizikai es kemiai folyamatok uvegek magas homersekletu feluletkezelese alatt, Epitoanyag, 1978, **30** (7), 241.
6. A. A. Belyustin, I. S. Ivanovskaya and G. V. Baranova, Effect of Heat Treatment on the Composition of Surface Layers in Lithium Silicate Glass Exposed to Acid and Salt Solutions, Glass Physics and Chemistry, 2002, **28** (2), 103.
7. V. Sharagov, O. Azarenko, Analysis of surface layers of industrial glasses, Proc. of Conf. „Glass in the New Millennium, Challenges and Break-through Technologies". ICG Annual Meeting 2000. Amsterdam, 2000. Session PS 4, CD-ROM, PS 4.3, p. 1.
8. V. Sharagov, O. Azarenko, G. Lysenko, Section etching of surface layers of container colorless glass, Romanian Journal of Materials, 2009, **39** (3), 212.
9. P. Baltă, Nano-heterogeneous structure of oxide glasses, Romanian Journal of Materials, 2012, **42** (3), 264.
10. D. Radu, O. Dumitrescu, The structural caracterization of alkali-silica glasses at the sub-nanometric scale, Romanian Journal of Materials, 2010, **40** (1), 50.

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MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS

Challenging Glass and **COST Action TU0905 on Structural Glass** have joined forces in the organization of an international conference on the **Architectural and Structural Applications of Glass**.

The conference aims at gathering world class designers, engineers and researchers on the architectural and structural use of glass, and will take place **6 - 7 February 2014 at the EPFL** - Ecole Polytechnique Fédérale de Lausanne, in Lausanne, Switzerland.

Conference themes

The main theme of the conference is the Architectural and Structural Application of Glass, which embodies the structural application of glass in buildings and facades. Within this main theme, several subthemes are defined, which are listed below:

- Projects & Case studies
- Joints & Fixings & Adhesives
- Strength & Stability
- Laminated Glass & Interlayer Properties
- Hybrid & Composite Glass Components
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- Curved & Bended Glass
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