CORROSION RESISTANCE OF COATED AND UNCOATED MATERIALS IN THE GLASS INDUSTRY

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Abstract

The work deals with the research of materials based on Cr-Ni steels which are commonly used in the glass industry. The surface of these materials is in the permanent direct interaction with the molten glass. Moreover, this surface is exposed to aggressive environment which occurs as a result of pre-heat by open flame, lubrication by oils and it can even occur on the basis of diffusion of other elements. If there is the occurrence of oxidation products on the surface, it means unacceptable quality of glass products and this causes defects relating to insufficient quality of products.

The work is based on proposed approaches including the influence of the surface to eliminate or to delay its occurrence. Proposed and performed corrosion tests of these materials can help from the aspect of decision for the selection of optimum surface of materials under the stress (glass moulds and glass pre-moulds). Therefore, it is very important to obtain information on behaviour for uncoated and coated material in a simulated corrosive environment.

Keywords: corrosion resistance, corrosion tests, coating, glass mould, glass pre-mould

1. INTRODUCTION

Thermally loaded components operating in corrosive - aggressive environment in the glass industry which accelerates the degradation process of materials, thereby reducing the overall lifespan.

The experiments made on the supplied samples were based on analysis of operating corrosion damage of steel samples 1.4016 and they were focused on the nature and extent of surface changes. The simulation of corrosive settings were performed on the prepared samples. All corrosion tests were carried out according to the standards.

Formulation of the problem:

To evaluate the change of structural surfaces in aggressive corrosive setting and the impact of structural inclusions on acceleration of corrosion process.

The evaluation methodology

Investigation of extent and type of damage is based on the metallographic evaluation of damaged sample surfaces from specific parts. Structural and phase characteristics were observed in transverse and longitudinal cuts of the sample depending on the rolling direction. Selection of materials is shown in Fig. 1. This material was subjected to the corrosion tests in the corrosion chamber.
Corrosion chamber

Corrosion tests were carried out in the corrosive environment of 5% NaCl on the corrosive diagnostic device Gebr. Liebisch S 400 M - TR with the parameters given in Tab. 1.

<table>
<thead>
<tr>
<th>Parameters of corrosion chamber</th>
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<tr>
<td>Volume of corrosion chamber</td>
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<tr>
<td>The temperature range of the corrosion chamber</td>
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<tr>
<td>The temperature range of the spray solution</td>
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<td>Consumption of the test solution</td>
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<td>Electric input</td>
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2. EXPERIMENTAL PART

Experimental evaluation was based on operating samples which were gradually chemically cleaned from the corrosive fumes. The basic material showed typical partial heterogeneity of ferrite grains - Fig. 2 and Fig. 3.

Fig. 2 Basic material 1.4510 in the central region
Fig. 3 Basic material 1.4510 at the surface

Operational damage of the material surface 1.4016 is documented in Fig. 4 and Fig. 5. Identified layer is mainly composed of oxide coating without linking with a surface of the evaluated material. Gradual surface cleaning resulted in almost complete elimination of the layer. Primary discontinuities are evident on the
metal sheet surface in the rolling direction. Due to the extent of corrosion attack these areas can be considered as initiating centres of degradation, that gradually passed into the base material.

Areas exposed to aggressive setting have obvious connection with baseline material surface. In all evaluated areas where intense surface damage was observed, material discontinuities were also documented on the surface associated with the local occurrence of carbide phases directly near the subsurface. Surface damage can be characterized as an unequal, locally initiated corrosion attack, that follows the state of the components surface. This defect does not have the character of a typical flat initiated pitting. Cavity morphology is caused by structural heterogeneity in the most damaged surface areas. Release of carbides allows penetration of corrosion into the internal volumes previously damaged material. In the immediate vicinity of corrosion cavities formation, the micro-volumes of decohesion after falling out of carbide phases without corrosive attack were also found.

This effect indicates the presence of a more complex phase spectra that differ in their relationship to the chemical stability of steel. Specific mechanism of corrosion damage is related to the heterogeneity of applied steel.

2.1 Microstructural analysis of the material 1.4016

The typical structure of steel 1.4016 which was to replace material 1.4510 is shown in Fig. 6 where a carbide chain was detected. Generally, from metallographic analysis in longitudinal cut shows that representation as well as distribution of carbide phases is preserved even across the whole cross-section sheet. The frequency of this phase does not decrease towards the surface and sometimes occurs the "collision" directly with the surface layer, which results in surface imperfections. The cause of typical decohesion of matrix are in – row excluded carbides that are in detail presented in Fig. 7.

Experiments showed that there was no distribution along the grain boundaries. Occurrence along the grain boundary and across the area in the interior in comparison with the occurrence in lines (in the rolling
direction) is negligible. Due to the observed relation with uneven corrosion surface damage, all occurring phases and their principled relationship with the local loss of corrosion resistance of steels were analyzed in detail.

Chemical microanalysis demonstrated that they are chromium carbides (in accordance with independent laboratory), which means that their occurrence induces chemical heterogeneity in the vicinity. There is a depletion of chromium, which is accompanied by a decrease of the corrosion resistance in these affected microlocations. The effect is very closely located because the layer does not reach over 2μm under the conditions of measurements.

Metallography confirmed the presence of in – row excluded inclusions. Chemical microanalysis show that they are complex oxide inclusions. The typical character of the complex oxides distribution is presented in Fig. 8 near more coherent lines of chromium carbides.

Occurrence of oxides in comparison with carbides was significantly lower and their exclusion was associated with significantly more serious matrix incoherence. In case of exclusion of more coherent line these complex oxide inclusions were source of continuous discontinuities that developed during rolling. The characteristic in – row exclusion and results of detected spectrum of inclusion type provides Fig. 9. Moreover, a crack creating occurred in this case.

![Fig. 8 Occurrence of complex oxides](image1)

![Fig. 9 Decohesion of matrix around complex oxides](image2)

From the structural material analysis, discontinuities ("the separating layers") generated in the vicinity in comparison with volumes of surrounding material away from defects, it shows that the damage of the surface do not have to be connected with more extensive non homogeneity of structural and chemical nature of the matrix.

Oxide inclusions were also observed in supplied samples of the material 1.4016. In terms of impact on the material quality, it is the same mechanism when in – row exclusion of oxides leads to matrix decohesion even to continuous discontinuities in the rolling direction. In the case of surface identified defect, the exclusion of these inclusions was done in a way of cluster in the surface layer. The load of this layer in rolling process subsequently led to a gradual redistribution of inclusions and isolation in this way contaminated layers accumulated in one location.

When it comes to the corrosion, the negative impact of damage lies in non compactness as well as in "mechanical" damage of the surface. This place belongs to the strong corrosion initiation, when it accumulates moisture and aggressive fumes from the environment in a such way damaged surface.

### 2.2 Microstructural analysis of the material 1.4510

To above mentioned evaluation results of the material 1.4016, in the supplied material sample the analysis was aimed to microcleaness evaluation, especially in the extent and distribution of contamination.

Surface distribution of inclusions was detected in the characteristic rate of contamination by non-metallic inclusions and this means definitely different character in contrast with in – row exclusion of the material 1.4016.
Identification by the chemical microanalysis showed that they are almost titanium nitrides - **Fig. 10.** Nitride distribution is accompanied by oxides excluding – they are complex, very fine oxides, often in direct combination with nitrides, which incidence in examined sample in comparison with occurrence of carbides was very low.

Occurrence of clusters of oxides complex (which evoked microscopic discontinuities in the material 1.4016) did not occur in the extent that would significantly reduce the material quality e.g. the unique cluster documented in **Fig. 11.**

![Fig. 10](image1.png)  ![Fig. 11](image2.png)

**Fig. 10** Nitrides in material 1.4510 – detail  **Fig. 11** cluster oxide inclusions in material 1.4510

From the whole range of the contaminants occurred, the oxide inclusions were observed in negligible rate. Occurrence of carbides in the locality was not observed in a significant extent - in any typical relation to the structural steel construction (in – row, surface or along the grain boundaries).

By detecting the carbide presence in the material 1.4510 in the comparison with the material sample 1.4016 it can be concluded the negligible effect on the corrosion resistance.

From the above mentioned evaluation of selected Cr-Ni materials which covered corrosion resistance there can be evaluated the following conclusions.

3. **CONCLUSIONS**

1. Surface of materials based on Cr-Ni steels, which interacts with the hot glass melt and simultaneously is exposed to aggressive environment not only affects the corrosion properties but also the strength characteristics of these materials.
2. Steel structure consists of ferrite grain mostly with non uniform size (if structure is finer, corrosion resistance is better) with the occurrence of the intermediate phases based on chromium carbides which affect corrosion resistance of ferritic steels.
3. Ferritic steel grains 1.4016 are elongated in the rolling direction which means that the texture after plastic deformation is maintained.
4. The occurrence of in –row ferrite shows large degree of deformation, which is retained in these steels and that leads in more stress in the material and reduced corrosion resistance.
5. State of stress ferritic structure is penetration residual and thermal stress, that can be amplified by the corrosion in the surface layers. This may occur by the formation of limit state deformations and violations.
6. In the case of occurrence by intermediate phases filled cavities, it is assumed that there will also be changes in the corrosion resistance of operationally exposed materials.
7. If the surface of the supplied materials is broken in any manner (by the straightening, welding, assembly), we can predict more tenseness in the subsurface layers leading to the initiation of cracks and other damage.
8. Also corrosion tests showed that in the areas of material discontinuities, more corrosive attack it occurred in comparison with the surrounding less damaged structure.

9. Ferritic Cr-Ni steel is very sensitive to any notches on the surface. The transition temperature will depend on compliance of the chemical composition, grain size and cleanliness of the structure.

Based on the comparison of the surface quality of supplied materials with etalon it can be clearly said that it is a big difference in a quality and that there will be a need to consider their use for glass materials. We recommend material 1.4510 based on the corrosion tests. When designing components that are in contact with hot glass melt it is very important the structural material purity, because this can also be the initiator of corrosive attack.

LITERATURE:

