Effects of Ion Bombardment pretreatment on glass coating processes and post tempering

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1.- Ariño-Duglass
2.- Gencoa
3.- Zaragoza University
Glass processing company:

- 20 different processing lines.
- Manufacture of coatings on processed glass.
- Standard High-Performance coatings.
- Develop of special coatings design.
- Diverse business sectors.
GENCOA: Industrial plasma sources and equipment control

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- Planar Magnetrons
- Plasma Pre-Treaters
- Rotatable Magnetrons
- Reactive Gas Control
- Pulsed Effusion Cells
Zaragoza University:
Group of Photonic Technologies

From the Lab to the Industry & Society
Examples of coated glass projects

Serrano Tower - Madrid

La Defense - Paris
Examples of coated glass projects

Skylight – Madrid New City Hall
Examples of coated glass projects

BP4 Canary Warf – London

Hotel Catalonia – Barcelona
Examples of coated glass projects

1. - CAF high-speed train.
2. - New Spanish regional trains.
3. - Talgo High-speed Mecah-Medina link. Saudi Arabia
• Most architectural glazing are based on standard coatings, applied on fresh float glass.
• Some architectural designs require non-standard coatings or to apply the coating on more special glass.
• In these cases coating must be applied on glasses that have been treated in several processing steps.

Initial glass processing:

Cutting

Edge polishing

Copper and gold coating developed for singular projects.
Silkprinting:

- Enamel deposition by silkscreen
- Drying at 150 °C
- Fusing/Vitrification at 600 °C
Laminated glass:

- Two glass panes adhered with plastic interlayer (Polyvinyl Butyral)
- Glass surfaces pressed by nip-rollers
- Autoclave cycle at 140ºC and 10bars.
Tempered glass:

1. Loading table in horizontal.
2. Heat glass up to 620ºC by IR radiation and forced convection.
3. Cool down by air pressure jets.
Coating on processed glass:

- Glass cleaning by industrial washer.
- Glass size up to 3600 x 2540mm.
- Magnetron sputtering PVD

Typical coating structures:

Spectral transmission of architectural coated glass:
Coating after glass processing steps

Glass surface quality not as recently produced float glass.

Standard glass cleaning is not enough.

Typical defects:

- Drying marks (from washing)
- Pinholes
- Loss of adhesion
- Scratches
- Surface contamination
Economic evaluation of coating rejects:

<table>
<thead>
<tr>
<th>Description</th>
<th>Number of units</th>
<th>Square meters</th>
<th>Economic lost value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ariño Duglass coated glass annual production</td>
<td>78.3 k</td>
<td>131.2 k</td>
<td>128 k€ (138 kUSD)</td>
</tr>
<tr>
<td>Rejections due to coating defects on processed glasses with strong surface modification (tempering, laminating, etc.). Heavy processing.</td>
<td>1875 2.40%</td>
<td>4261 3.25%</td>
<td></td>
</tr>
<tr>
<td>Rejections due to coating defects on glasses normal / light processing (cutting and grinding)</td>
<td>918 1.17%</td>
<td>1.8 k 1.37%</td>
<td>27 k€ (30 kUSD)</td>
</tr>
<tr>
<td>Total rejections due to coating defects</td>
<td>2.8 k 3.57%</td>
<td>6.1 k 4.62%</td>
<td>155 k€ (167 kUSD)</td>
</tr>
</tbody>
</table>
To avoid these drawbacks the effect of ion pretreatment on industrial glasses for coating has been studied.

IM Linear ion source has been used for glass surface treatment before coating.

The study has been made based on a typical solar control coating.
Linear Ion Sources are effective at removing atomic layers of contaminants without adding roughness
R&D semi-industrial Sputtering System (Korea VCT) – @ University of Zaragoza:

- Process chamber with 8 magnetron sources (100 mm x 600 mm targets)
- Speedflo - Plasma emission monitor for stable reactive deposition
- Linear Ion Source for surface pretreatment
**Thin film structure:** Glass / SiAlN x (20nm)/ NiCr (40nm)/ SiAlN x (40nm)  
Deposited in R&D Sputtering system (Applied Physics Dep., University of Zaragoza)

**Process condition:**
- Base pressure: $7 \times 10^{-6}$ mbar
- Ion beam pre-treatment: 2 kV, Ar flow 50 sccm (1 pass @ 45 cm/min)
- SiAl target: reactive mode. N$_2$ flow ~100 sccm, Ar flow 100 sccm. Power: 2.5 kW  
  (Layer 1: 1 pass @ 70 cm/min – Layer 3: 1 pass @ 35 cm/min)
- NiCr: metallic mode. Ar flow 200 sccm. Power: 2.0 kW (1 pass @ 105 cm/min)

**Optical properties:**

<table>
<thead>
<tr>
<th>Light Trans.</th>
<th>13.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Reflec. (glass side)</td>
<td>41.8%</td>
</tr>
<tr>
<td>Light Reflec. (coat side)</td>
<td>24.1%</td>
</tr>
</tbody>
</table>
Taber abrasion test

- Abrasion resistance of coatings
- Taber Abrading wheel CS-10F
- Rolling and rubbing combination
- Load: 5 N
- No. Cycles: 300
- Comparative results of coating with and without ion beam pre-treatment

**Sample without ion-beam pretreatment**

**Sample treated by ion beam**
Elcometer abrasion test (ISO 11998)

- Abrasion resistance of coatings
- Rubbing in wet conditions
- Load: 100 gr.
- No. Cycles: 500
- Comparative results of coating with and without ion beam pretreatment

Sample without ion-beam pretreatment

Sample treated by ion beam
Coating adhesion is extremely important if a tempering process is performed after coating.

Glass is heated to 620 °C in 240 s
Quick cooling down to ambient temperature (less than 100s)
Tempering process video

Architectural & Automotive Glass

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Several coated glass samples (350x350mm and 6mm thickness) have been submitted to a typical tempering cycle.

Same coating structure: Glass / SiAlNₓ / NiCr / SiAlNₓ

A comparative study has been made between samples with and without ion beam pre treatment.

<table>
<thead>
<tr>
<th>Sample not treated by ion beam</th>
<th>Sample with ion-beam pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Sample not treated image" /></td>
<td><img src="image2.png" alt="Sample treated image" /></td>
</tr>
</tbody>
</table>

(Images using a Metalographic Olympus BX60 microscope – in reflection) x 200
Parallel on-axis in-lens secondary electron detection

Sample not treated by ion beam

![SEM image of sample not treated by ion beam]

Samples without ion beam pretreatment show a hazy reflection.

Due to small bubbles (5 µm) in the coating.

Sample with ion-beam pretreatment

![SEM image of sample with ion-beam pretreatment]

After the tempering process no visible defects were detected on the coating.

SEM analysis confirm the good state of the coating.
Angle selective backscattered Detector (AsB) for crystallographic contrasts

Ion-beam treated. Tempered sample – NO DELAMINATION

Si₃N₄
NiCr
Si₃N₄

Glass substrate

Results

EHT = 3.00 kV
ESB Grid = 1500 V
I Probe = 400 pA

WD = 3.1 mm
Mag = 38.00 K X
Pixel Size = 2.938 nm

Signal = 1.0000
Signal A = ESB
Signal B = AsB

Date: 13 Apr 2015
File Name: CT_pulida_04.tif
Tempered sample, no ion-beam pretreatment
MIXTURE OF ADHERENT & NOT ADHERENT ZONES

Angle selective backscattered Detector (AsB) for crystallographic contrasts

Results
Tempered sample, no ion-beam pretreatment

Zone where the coating was detached from substrate

Angle selective backscattered Detector (AsB) for crystallographic contrasts
Energy selective backscattered. Cross-section

Adhesion loss between glass and coating

Glass substrate

Coating
Adhesion loss between glass and coating

Glass substrate

Coating

Results

Parallel on-axis in-lens SE. Cross-section
No significant chemical differences between areas.
No chemical reactions due to the high temperature cycle.
No chemical differences between ion-beam treated and non treated after tempering process.
No significant oxidation/chemical reaction.
Several zones where coating has been peeled off

Confirmation by X-ray micro analysis.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Si</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_5Kv</td>
<td>55.94</td>
<td>8.39</td>
<td>2.09</td>
<td>33.58</td>
<td>100.0</td>
</tr>
</tbody>
</table>

All results in weight%
Conclusions:

- Ion beam pretreatment presents great interest for large area glass coatings.
- Reduction of coating defects.
- Increase of abrasion resistance.
- Essential for coatings subjected to tempering process.
- Increase of economic profit.
- Return of investment 6-9 months
Thank You

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