

Glass Coating by Atmospheric Flame Spray Nanoparticle Deposition

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Abstract

This paper presents results of a novel means for applying colour, functional coatings and surface modifications to glass and other vitreous substrates. The method incorporates atmospheric flame-based synthesis of metal and/or metal oxide nanoparticulate material and deposition thereof on desired surfaces. The results presented refer to soda-lime glass that was coloured with oxides of cobalt. The samples were characterised by spectrophotometry to reveal their transmission spectrum and by laser ablation mass spectrometry to determine the cobalt doping concentration profile. The results show that the transmission spectrum of the surface coloured glass is comparable to that of body-tinted glass. The cobalt doping profile exhibits a smooth concentration gradient of cobalt in the upper surface region of the glass.

Keywords: atmospheric, glass coating, nanoparticle

1. Introduction

The market for plain flat glass is close to saturation. The need for properties that add value to manufacturers' glass products is factual and increasing. Properties sought after are colour (either body-tinted or surface coated), solar control, Low-E, self-cleaning, sound abatement and reflection control, to name but a few. During the past decades, several means for applying special properties have been developed, and hence a variety of coating methods are used by the glass industry today, *e.g.*, chemical vapour deposition (CVD), spray pyrolysis, physical vapour deposition (PVD) methods such as magnetron sputtering, sol-gel coatings etc. These techniques are either implemented as on-line (continuous) or off-line (batch) applications.

With this paper, the authors present a new means at hand for coating and surface treating glass either on- or off-line. The method, already known in scientific contexts as liquid flame spray deposition (LFS), is patented [1] and currently utilised in production [2] in the optical fibre and laser industries. In this context, however, it is called Direct Nanoparticle Deposition (DND). In essence, LFS is an atmospheric flame-based nanoparticle synthesis process. The flame, which predominantly is a turbulent hydrogen-oxygen flame, is fed with the precursor chemicals as liquid, vapourous or gaseous feedstock. The precursor chemicals subsequently undergo thermo-chemical and –physical reactions, ultimately leading to the synthesis of nanosized particles. The synthesis route follows the process steps of nucleation-condensation controlled gas-to-particle synthesis [3].

Liquid flame spraying, as a means for particle generation, has been widely studied and documented by several research groups [4-7]. Applying LFS to colouring glass, *i.e.*, hand-blown art- and tableware, is one of the early applications of LFS [8-9]. However, taking glass colouring further and implementing it in the manufacturing of float glass has not yet been done. The current approach is of interest to the glass manufacturing industry, because LFS produces a durable and chemically stable colour, which is inside the glass, not on it, and also, LFS enables instantaneous change of colouring or coating materials during production. The latter means a considerable reduction in the amount of lost glass and labour when, *e.g.*, changing the colour of conventionally body-tinted float glass. In addition, the versatility of the process, in terms of product species, enables (and requires) new thinking and approaches to coating glass.

In applications where liquid flame spray deposition is used for glass colouring, surface modification or similar, the process is henceforth designated nHALO, short for Hot Aerosol Layering Operation.

2. Experimental

2.1 Sample material

This study concentrates on cobalt doping of soda-lime glass using liquid flame spray deposition. The main focus of interest was on determining the concentration profile and doping level of cobalt after colouring treatment. Square samples measuring 150 × 150 mm were cut from 4 mm thick clear float glass. Table 1 presents the chemical composition of the substrate material.

Table 1

Chemical composition of the glass used in the experiments. All figures in weight percentage (wt-%).

| | SiO ₂ | NaO ₂ | CaO | MgO | Al ₂ O ₃ |
|------------|------------------|------------------|-----|-----|--------------------------------|
| Test glass | 73 | 15 | 7 | 4 | 1 |

The glass samples were cleaned with ethanol before being laid horizontally on a particulate board used as a sample carrier. The laboratory nHALO coating chamber was not equipped with a tin bath for glass supporting purposes. Instead, the sample carrier was modified by making a square cavity in the middle, in other words, the samples were supported from their periphery only. This was to avoid optical distortion that otherwise would occur during heating when the glass would slump and copy the surface features of the sample carrier it was laid on. The glass samples were coated on their tin-free side.

2.2 Sample coating

The liquid flame spray burner was set up to coat the glass samples in vertical direction, flame downwards. The burner was supplied with hydrogen (H_2) and oxygen (O_2) gases for the flame and nitrogen (N_2) for control of the flame geometry. The flame was kept slightly rich on hydrogen during the trials. Raw materials for colouring were fed as a liquid feedstock mixture containing cobalt(II)nitrate hexahydrate and methyl alcohol. The dilution ratio used was 1 part cobalt nitrate + 40 parts methyl alcohol per weight.

Two samples were coated for this experiment. Sample A was coated to give a definite blue colour, yet retaining full transparency. Sample B was coated to give a less vivid colour but again full transparency, as a reference point to sample A. The glass samples were placed on sample carriers at ambient temperature and moved into the pre-heating section of the coating chamber. The resistively heated pre-heating section was kept at $750\text{ }^\circ\text{C}$ during the experiment. The temperature of the glass samples prior to coating was monitored by a pyrometer. The glass was allowed to heat until the predetermined glass coating temperature was reached, after which the glass was moved into the coating chamber for coating. Initial coating temperatures for sample A and sample B were $700\text{ }^\circ\text{C}$ and $675\text{ }^\circ\text{C}$, respectively.

Once the coating temperature was reached, the burner coated the sample with a scanning motion, traversing across the glass surface back and forth. The burner traversing velocity was the same for both samples. Between every sweep made by the burner, the glass samples were moved stepwise forward, thus feeding uncoated glass for every burner sweep. The step sizes for sample A and sample B were 10 mm and 20 mm, respectively. Hence, sample A was coated with twice the amount of material compared to sample B. Immediately following coating, the samples were placed in a post-heating furnace at $500\text{ }^\circ\text{C}$ for 30 min.

2.3 Transmission spectrum measurements

Transmission spectra were measured for sample A and sample B with a customary UV-spectrophotometer setup. Border wavelengths were 350 and 800 nm and the monochromator stepping was set at 20 nm. Optical measurements were referenced against air. Transmission characteristics were determined from transmitted power through the sample. Reflectance is thus included in the transmission results.

2.4 Doping concentration measurements

The concentration of the coating material was determined by measuring the concentration profile of cobalt in the glass matrix. As mentioned earlier, the colouring effect of nHALO product species is based on their migration into glass. Therefore, the colorant concentration was expected to be highest at or just below the surface of the glass and lowest at a depth of some tens or hundreds of microns.

Cobalt profiles were measured with a Perkin-Elmer Sciex ICP Elan DRC Plus laser ablation mass spectrometer (LAMS). The ablation process was monitored with a CCD camera microscope. The ablation beam was vertical and $4\text{ }\mu\text{m}$ in diameter. As the beam was in the same size range as the actual profile depths, special care had to be taken in order to successfully distinguish the actual profile from the measurement data.

Two kinds of profile measurements were performed. The cobalt concentration was measured by probing both the sample's cross-sectional side and from the surface downwards. Samples were attached vertically for the cross-sectional measurement. The measurement was performed with a single scan in a direction perpendicular to the sample surface line. For the surface scans, the samples were attached horizontally, and the measurement consisted of repeated ablations from the same region in order to collect information about the doping profile. The ablation region was a line, over which the measurement signal was averaged. The LAMS surface scans were made with a $15\text{ }\mu\text{m}$ laser spot size and $5\text{ }\mu\text{m}/\text{sec}$ scanning velocity. The cobalt concentration was averaged over each scan, and scans were repeated in order to obtain a comprehensive depth profile. The resulting concentration was calibrated over a standard sample NIST 612 [10].

3. Results

3.1 Sample coating

Under visual inspection both samples were clean with characteristic bluish tint due to the presence of cobalt colorant. Sample A had a deeper colour but was fully transparent, as expected. No visual haze was present. With an optical microscope it was possible to detect a moderate amount of crystalline regions on the surface of sample A.

3.2 Transmission spectra

The transmission spectrum of sample B is presented in Figure 1. It is worth noting that the spectrum is referenced against air (no sample). In addition to the measured data in Figure 1, an effort has been made to match the measured spectrum with one obtained by calculated absorption characteristics of Co_3O_4 -coloured soda-lime glass with optical properties such as tabulated in reference [11]. In the calculated example a 4 mm thick soda-lime glass substrate is cascaded with a $40\text{ }\mu\text{m}$ thick coloured silica layer. The colourisation includes an erfc-type cobalt concentration distribution and a surface concentration at a level of 32 mg/g.

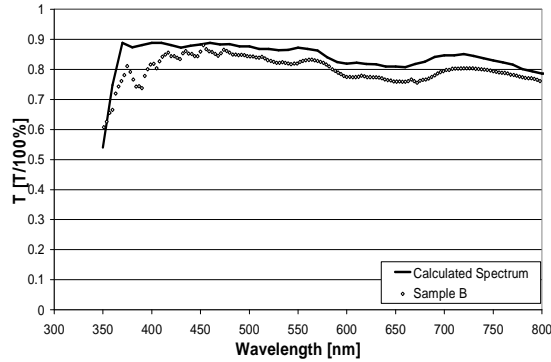


Fig. 1. Transmission spectrum of sample B. The solid line represents a calculated reference spectrum.

The calculated transmission spectrum and the measured data fit well together after adjusting the characteristic diffusion length of the calculated example to $4.0\ \mu\text{m}$ in an erfc-type profile. Reflection was not taken into account in the calculations, and thus there is a vertical difference between the two curves in Figure 1. From the results one can clearly see, that the measured transmission spectrum can easily be interpreted using documented characteristics of Co_3O_4 -coloured glass, even when the colorant is introduced to the surface layer only.

3.3 Doping concentration

During laser ablation of the glass samples, it was observed that the ablation itself extracted material from the sample in a non-uniform manner. Ablation grooves in sample B were analysed with optical microscopy, and it was found that after six scans roughly 70% of the groove was ablated to a depth of $\approx 6\ \mu\text{m}$, while 30% was ablated deeper, to a maximum depth of $\approx 18\ \mu\text{m}$. This means an average of $1.6\ \mu\text{m}$ ablated depth per scan at the set laser power level. A typical doping profile needed approximately ten repeated ablation scans with this measurement method. During surface scanning of sample A, it was observed that cobalt was being ablated readily from specific regions along the ablation line, thus supporting the view that the crystallites observed on the surface of sample A were indeed rich on cobalt. This, together with the uneven ablation, led to the assumption that ablation excavated more readily the regions with an excessive amount of cobalt, leaving regions of pure silica less ablated. As a result, the averaged mass spectrometric signal was cobalt-rich during the first surface scans, resulting in a concentration profile with a seemingly smaller diffusion length.

Cross-sectional measurements were done in regions where the side cut was smooth under microscopic view, and thus less susceptible to crystallite effects. Figure 2 presents the measured LAMS signal from a cross-sectional scan of sample A. The first $4\ \mu\text{m}$ of sample surface have been screened by the laser beam diameter, and yet a profile is

clearly obtained. The estimated diffusion length according to an erfc-type fit is about $6\ \mu\text{m}$.

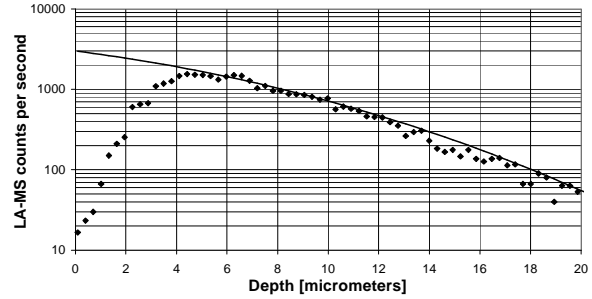


Fig. 2. Cobalt concentration of sample A, cross-sectional view. The solid line shows an erfc-type fit with a characteristic diffusion length of about $6\ \mu\text{m}$.

A cross-sectional LAMS signal of sample B is depicted in Figure 3. The calculated diffusion length was about $4\ \mu\text{m}$.

By assuming an erfc-type concentration distribution of cobalt in the coloured glass, we can cross-check the obtained profiles numerically by dividing the erfc-type profile into $1.6\ \mu\text{m}$ slices and integrating over the slices in order to replicate the ablation scans. The results of this procedure are shown in Figure 4. A surface concentration that yields a good fit to the measured results was found to be around $32\ \text{mg/g}$, or $3.2\ \text{wt-\%}$, for sample B. However, the best fit was obtained using a $2\ \mu\text{m}$ diffusion length instead of the $4.0\ \mu\text{m}$ suggested by the cross-sectional profile scan. This is, nonetheless understandable with the earlier observed non-uniform excavation during laser ablation

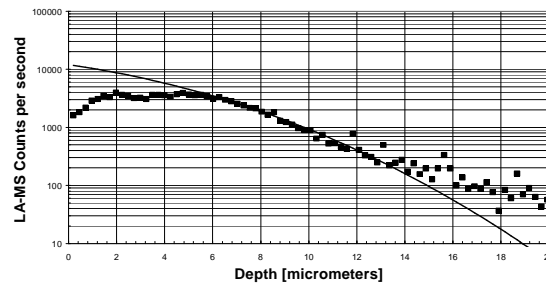


Fig. 3. Cobalt concentration of sample B, cross-sectional view. The solid line shows an erfc-type fit with a characteristic diffusion length of about $4\ \mu\text{m}$.

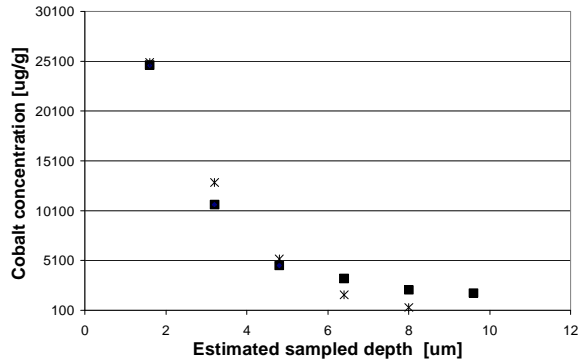


Fig. 4. Measured cobalt concentration (black squares) of sample B (surface sample). Calculated values from an erfc-type profile are shown as stars.

4. Discussion

The optical absorption of cobalt oxide in soda-lime glass is a subject that has been widely studied. Bamford [11] has published numerical data on optical absorption coefficients versus added Co_3O_4 per wt-% in soda-lime glass. It is therefore interesting to compare transmission spectra from traditional mixed body-tinted glass melts with those obtained by atmospheric liquid flame spray deposition (nHALO), which inherently is a surface treatment with only moderate penetration into the glass matrix. As shown in Figure 1, the nHALO treated glass surface replicates surprisingly well the transmission spectrum of traditionally cobalt coloured glass. Moreover, the measured and calculated concentration levels and profiles compare adequately.

5. Conclusion

nHALO coloured samples were studied using laser ablation mass spectrometry for determining the cobalt concentration profile. Diffusion lengths were found to be 6 and 4 μm in sample A and B, respectively. The cobalt concentration was around 3.2 wt-% on the surface of sample B. The measured transmission spectrum of sample B was in accordance with a calculated estimate, supporting the validity of the measured and calculated concentration profiles of cobalt. LAMS measurements were successfully applied to investigation on concentration profiling of cobalt in silica. However, care should be taken in order to minimise errors due to non-uniform ablation of material.

References

- [1] J. Tikkanen, V. Pitkänen, M. Eerola, M. Rajala, Finnish Patent No. 98132, 1998.
- [2] M. Hotoleanu, P. Kiiveri, S. Tammela, S. Särkilahti, H. Valkonen, M. Rajala, J. Kurki, K. Janka, in: R. Herber, D.W. Faulkner (Eds.), Proceedings of the 7th European Conference Networks & Optical Communications (7th NOC), Darmstadt, Germany, June 18-21, 2002, p. 547.
- [3] S.E. Pratsinis, Proceedings of the International Symposium on Multiphase Flow and Transport Phenomena (ICHMT MFTP 2000), Antalya, Turkey, November 5-10, 2000.
- [4] J. Karthikeyan, C.C. Berndt, J. Tikkanen, J.-Y. Wang, A.H. King, H. Herman, NanoStructured Mats, 8 (1997) 1.
- [5] J. Tikkanen, K.A. Gross, C.C Berndt, V. Pitkänen, J. Keskinen, S. Raghu, M. Rajala, J. Karthikeyan, Surface and Coatings Techn. 90 (1997).
- [6] H. Keskinen, J.M. Mäkelä, M. Vippola, M. Nurminen, J. Liimatainen, T. Lepistö, J. Keskinen, J. Material Research, 19 (2004) 5.
- [7] J.M. Mäkelä, H. Keskinen, T. Forsblom, J. Keskinen, J. Materials Science, 39 (2004) 8.
- [8] K.A. Gross, J. Tikkanen, J. Keskinen, V. Pitkänen, M. Eerola, R. Siikamäki, M. Rajala, J. Thermal Spray Techn. 8 (1999) 4.
- [9] J. Tikkanen, Ph.D. Thesis, Tampere University of Technology Publications 266. Tampere University of Technology, Finland, 1999.
- [10] National Institute of Standards & Technology Certificate of Analysis, Standard Reference Materials 612, Trace Elements in a Glass Matrix (3 mm wafer), NIST, Gaithersburg, 1992.
- [11] C.R. Bamford, Colour Generation and Control in Glass, Glass Science and Technology 2, Elsevier North-Holland Inc., 1977, New York, ISBN 0-444-41614-5.