3. Bhattamishra, A.K. and Banerjee, M.K., Zeitschrift fuer Metallkunde/Materials Research and Advanced Techniques, 1993, 84, 734-736.

4. Bethencourt, M., Botana, F.J., et al., Corrosion Science, 1998, 40, 1803-1819.

5. Campestrini, P., Terryn, H., Hovestad, A., and Wit, J.H.W.d., Surface Coating and Technology, 2004, 176, 365-381.

6. Schmidt, H., Müller, P., et al. Sol-Gel derived Nanocomposite Materials for Corrosion Protection of Aluminium Alloys. in Eurocorr. 2000. London.

7. Mansfeld, F., Wang, V., and Shih, H., Journal of the Electrochemical Society, 1991, 138, L74-L75.

8. Schmidt, H., Jonschker, G., and Langenfeld, S. (INST NEUE MATERIALIEN), DE 19813709 (27.03.1998) „Verfahren zum Schutz eines metallischen Substrates vor Korrosion“

9. van Laar, J.A.W., Deutsche Farbenzeitschrift, 1961, 15, 56-67 and 104-117.

10. Zheludkevich, M.L., 2007, unpublished results

11. Szklarska - Smialowska, Z., Pitting Corrosion of Metals. 1986: NACE International. 431.

Annotation

The results presented here have also been published during the EUROCORR 2007.

Microstructure investigation of reflective coatings interference multilayers produced by sol-gel method

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1. Introduction

Reflective and antireflective coatings play an important role in different branches of industry like optical devices, solar panels, medical devices (endoscopes), architecture, etc. The reason for this is the increase or reduction of transmittance or reflectance of the surfaces to the desired values. Transmittance and reflectance have to be optimized at different wavelengths depending on the application of the products.

There are different methods to change the reflectance of the surfaces: a) reflectance of the surface can be increased by coating the surface with metal (Al, Ag); b) reflectance of the surface can be decreased by coating the surface with moth eye pattern (coating with micro roughness on the surface or etching of the surface); c) reflectance of the surface can be decreased or increased by coating the surface with interference multilayers (the layers contain low and high refractive index materials). This paper is focused on the interference multilayers for increasing the reflectance of glass substrate from 8% up to 80%.

Producing of interference multilayers for performance of high or low reflectance can be achieved by different technological coating methods, like PVD-, CVD- and sol gel methods.

In this paper, sol-gel method is chosen as a coating method. The reason for this selection is the economical point of view. In general, the sol-gel method does not require expensive vacuum equipments. This makes sol-gel systems popular for coating large substrates. Generally, for low to high optical performance, the sol-gel method is cost effective in comparison to the other methods, especially if stack firing is used. Nowadays, it is possible to coat the interference layers not only on the glass substrate but also on the plastic foils. In this paper, the interference layers are coated on glass substrates. The main motivation for this paper is to investigate the microstructure of five layers reflective coatings by high resolution transmission and scanning electron microscopes (HRTEM, HRSEM) regarding pores, micro cracks and crystallinity of nano particles inside the layers.

2. Experimental details:

2.1. Optical performance simulations

The design for a 5 layer reflective interference filter with a maximum of reflectance at 550 nm was elaborated by computer simulation (simulation software: TF calc, version 3.5). The appropriate refractive indices were measured experimentally (ellipsometry) at a single layer coating of SiO_2 and TiO_2 sols on the glass substrates.

2.2. Optical performance dip coating

At INM, coating solutions based on surface modified high (TiO_2) and low (SiO_2) refractive index nanoparticles have been developed [1]. These sols are well suitable for the preparation of interference multilayer systems on glass [2].

In order to clean the glass substrate, it was polished at first with CeO_2 and washed in a dishwasher with a detergent at a particular program for glass substrate.

The multi layer design was realized on glass substrate in size 21 x 29,7 cm² using a dip coating machine in a clean room. This technique allows the deposition of layers with the same thickness on both sides of a glass pane in one coating step.

After each coating step, the coated sheet was dried for 3 minutes at 120 °C. Finally, the whole stack (up to 5 single layers) can be fired in one step at 450 °C, so called stack firing [3]. (Stainless steel muffle, 0.5 m x 0.5 m x 0.5 m). This is a cost saving heating process compared to the single layer firing process [4]. The furnace was heated from 25 °C to 450 °C with a heating rate of 2.5 K/min, the temperature was held for 45 minutes at 450 °C and cooled down to 25 °C with an estimated rate of 0.7 K/min by switching off the heating and keeping the door closed over night.

The surface modified nanoparticles arrange themselves to very dense and smooth layers (average roughness < 10 nm [5]) during the film formation.

Coating thickness, refractive indices and reflectance loss were measured by UV-VIS-spectroscopy (Cary 5E spectrometer, VARIAN Australia, Pty-Ltd) and spectral ellipsometry (SOPRA, ES4G).

2.3. TEM investigation

For TEM specimen preparation, a cross- sectional specimen preparation method was used. The samples were cleaved with a diamond pen and were glued face to face on the coating sides with epoxy (Gatan), which hardened after 30 minutes at 100 °C. After cutting the glued sample by an ultrasonic driller in a cylinder form, it was fitted into the rigid brass tube. The glued sample in the tube was glued again with epoxy. Disks of approximately 500 µm thick were cut from the tube with diamond plate, polished, and dimpled to approximately 20 µm thickness in the center of the TEM specimens. They were then ion milled with an argon ion beam (Baltec RES 010), operating at 5 kV accelerating voltage on rotating specimens inclined to the argon beam (2°). Finally the specimens were carbon coated for electron conduction during TEM-investigation.

The microstructure and the microanalysis of the coated glass samples were examined by a field emission gun TEM (Philips CM200 FEG) operated at 200 kV, equipped with x-ray energy dispersive spectrometer (EDS).

2.4. SEM investigation

The microstructure and the microanalysis of the coated glass samples we examined and conducted by

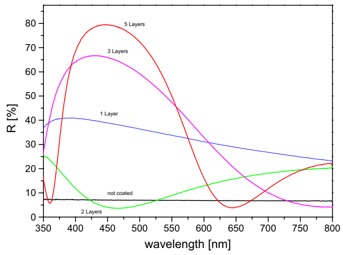

Fig. 1: The spectra of the glass substrate before coating, the single layer (H), two layer system (HL), three layer system (HLH) and five layer system (HLHLH) show the reflectance (R) versus the wavelength between 350 and 800 nm H: high refractive index, L: low refractive index.

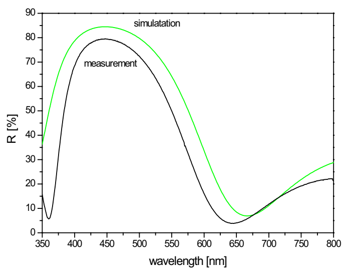

Fig. 2: Measured and simulated spectra of the five layer system (HLHLH) show in the reflectance (R) versus the wavelength between 380 and 800 nm.

HRSEM operated at 10 kV (JEOL 6400F), equipped with x-ray energy dispersive spectrometer (EDS), in planar and cross-sectional views. The cross-sectional views of multilayers were recordered at the broken samples. The planar views were recordered at the surfaces of the layers. All SEM samples were decorated with a very thin layer of gold coating (10 nm) for electron conduction.

2.5. Spectroscopic measurements

Refractive indices and reflectance were measured by UV-VIS-spectroscopy (Cary 5E spectrometer, VARIAN Australia, Pty-Ltd) and spectral ellipsometry (SOPRA, ES4G). Reflectance was measured at middle part of coated sample. For the determination of the refractive index of a single layer, a very thin layer was coated using dip coating method on the same type of glass substrate. The layer was thermally cured as described in part 2.2.

3. Results and discussion

3.1 Spectra

A five interference layer system was realized on a glass substrate by the deposition of TiO_2 (H) and SiO_2 (L) layers using a dip coating method in order to develop a high reflective coating in the visible range (H and L stand for high and low reflective material). The refractive indices of H-Sol (TiO_2) and L-sol (SiO_2) are 1.90 and 1.49 (at 550 nm) respectively. All glass substrates were coated on both sides. Figure 1 shows the spectra of the different coating systems. The single layer (H) increases the reflection in the whole visible range from 8% to about 30%, whereas the coating system of two layers (HL) produces an antireflective coating with 3% reflection at around 470 nm. A three layer system (HLH) increases the reflectance in visible region up to 67%. Four layer system produces an antireflective coating (HLHL). Finally, the system consisting of five layers (HLHLH) increases the reflection in the visible region to approx. 80% (at 450 nm).

Figure 2 shows the measured and simulated spectra of the five layer system (HLHLH). The real five layer system indicates a main maximum reflection value of 80% at 448 nm but the simulated five layer design has its main maximum of 84% at 448 nm. It can be supposed that this difference comes from a diffusion process at the phase boundary between the layers. In this case a refractive index

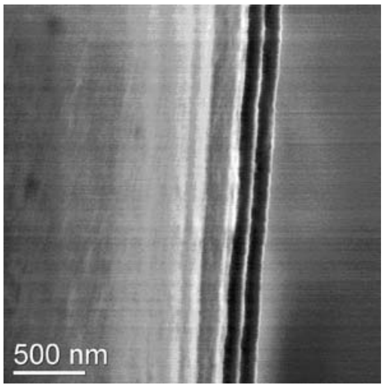

Fig. 3: Cross-sectional overview of the layers. Only two layers can be seen clearly. Coating thickness are around 100 nm, which can be exactly determind by HR-TEM.

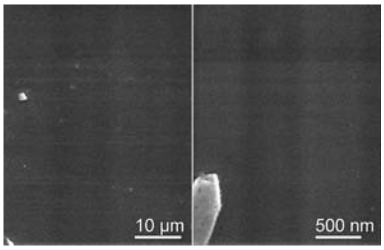

Fig. 4: An overview (a) and high magnified (b) SEM- micrographs of the surface last layer. There are no cracks or micro-pores on the sur face. The artefact particles on the surface are just a help to make sure that the images are in focus.

gradient should occur between the layers. One can verify this assumption through investigating the phase boundary by using transmission electron microscopy. Unfortunately, this multilayer coating is not proper for such an investigation of phase boundary interdiffusion because both sols (H and L) contain TiO_2 and SiO_2 nanoparticles. But in the near future, pure TiO_2 and pure SiO_2 nanoparticles are going to be used for sols H and L respectively. These pure layers should allow to investigate exactly the interdiffusion between layers using microchemical analysis by HRTEM.

SEM-investigations show that the coatings are very smooth and homogeneous. The SEM-micrographs of the surfaces prom first to forth layer look all alike as shown in figure 4. Both SEM- micrographs show that the surface is free of cracks and pores. The cross sectional SEM micrograph of the fracture surface did not show the five layers together (it could be that some layers are broken during sample preparation or they could not be brought to focus simultaneously). Nevertheless this micrograph reveals the approximate value of layer thickness. In order to know the exact thickness of the layers, it is necessary to make a very fine polished SEM sample or a thinned TEM sample.

The cross-sectional TEM micrographs (figures 5 and 6) show that the layers are very homogeneous and there are no pores or cracks in the layers. The coating thickness can be measured exactly. For the TiO_2 layers they were found to be 45, 49, and 55 nm respectively. The thickness of the two SiO_2 layers are very similiar around 65 nm. The diffraction patterns of the TiO_2 and SiO_2 layers (figure 6) indicate that they are made of crystalline and amorphous phases respectively.

Microanalysis of the layers are shown in figure 7. TiO_2 layers contain, as expected, small amounts of SiO_2 particles and also SiO_2 layers contain small amount of TiO_2 particles. Different variation of sols has shown that this chemical compositions results in very homogeneous layers when processed by the coating process.

4. Conclusion

It was shown that a system of five reflective layers can be produced by sol gel method with a stack firing as final heat treatment. The microstructure studies of the layers by HRTEM and HRSEM showed that there are no cracks or pores in submicrometer

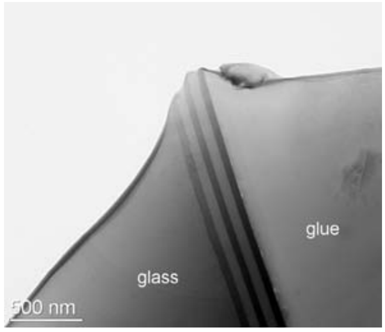

Fig. 5: TEM micrograph of cross sectional overview of the interference multilayers

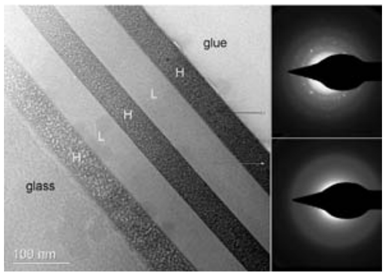

Fig. 6: High magnification of cross sectional view of multilayers by HR TEM. Dark layers are TiO_2 layers and bright layers are SiO_2 layers

size in and at the surface of layers and especially on the top layer. The thicknesses of TiO_2 and SiO_2 layers are in the range between 45-55 nm and 65 nm respectively. The crystalline phase of TiO_2 and amorphous phase of SiO_2 nanoparticles were observed by HRTEM. A small reflectance differences between simulated and real interfrerence multilayers could be originate from interdiffusion of TiO_2 and SiO_2 nanoparticles at the phase boundaries. This is an issue for the next investigation in which pure TiO_2 and pure SiO_2 layers have to be produced for such an investigation. The purity of layers may allow to investigate the phase boundaries with respect to interdiffusion in detail via michrochemical analysis by HR-TEM.

[1] DE 197 46 885; 23.10.1997, Nanostrukturierte Formkörper und Schichten sowie Verfahren zu deren Herstellung ; E. Arpac, H. Krug, P. Müller, P. W. Oliveira, H. Schmidt, S. Sepeur, B. Werner

[2] M. Mennig, P.W. Oliveira, H. Schmidt, Thin Solid Films, 351 (1999) 99-102

[3] DE 198 23 732A1; 27.05.1998, Verfahren zur Herstellung optischer Mehrschichtsysteme M. Mennig, P.W. Oliveira, H. Schmidt

[4] E. K. Hussmann, Key Engineering Materials Vol. 150, pp. 49-66, 1998

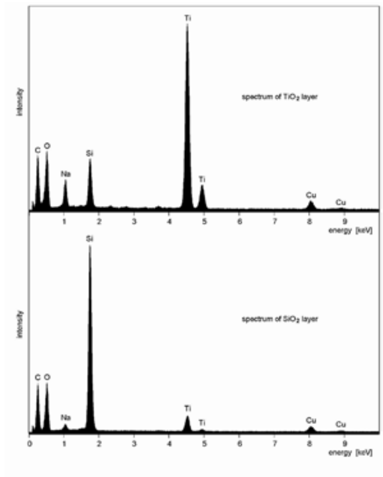

Fig. 7: Energy dispersive x-ray spectra of the TiO_2 and SiO_2 layers

Investigation on thermal and chemical stability of polymer based easy-to-clean nanocomposite systems

Ralf.Gerdes, Pamela Kalmes, Carsten Becker-Willinger

Abstract

Anti-adhesive coatings are of significant importance for many industrial processes such as pigment and paint production as well as also food processing industry, because they can help to significantly reduce the cleaning effort. For this reason, the amount of cleaning chemicals and waste water can be reduced, which should have a remarkable effect on the process costs. In this investigation abrasion resistant low surface free energy coatings based on fluoroalkyl group and SiC particles containing polyimides have been synthesised which show surface properties comparable to PTFE and can be coated like a paint on surfaces. Especially in food production processes a high chemical stability is required for coating materials to withstand the cleaning procedures which are used in order to maintain the hygienic situation in the production facilities. The investigations revealed a high abrasion resistance (weight loss approx. 12 mg after 1000 cycles taber abrader test) and a moderate chemical stability of the coating systems. A chemical attack by sodium hydroxide solution as