Durable Multilayer Thin Film Coating on Polycarbonate for Automotive Mirrors

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ABSTRACT

The automotive industry has embraced plastic as its preferred engineering material in many components, for example body panels, brackets and even brake pedals. One application which has not undergone this transfer is the rearview side mirror. In this case, the glass substrate is highly scratch resistant, cheap and easy to metallise. Glass does bring disadvantages, as it is dense, is hard to form complex shapes and is prone to shatter in the case of an impact. By shifting to a plastic substrate these limitations can be overcome. However, the durability of the plastic mirror must be enhanced to meet the specified performance of glass. This study reports on the development of a highly durable multilayer thin film coating on polycarbonate. Interestingly, the conventional wisdom of placing the metal layer underneath a transparent protective layer was found to be problematic and a novel approach was required. A sputtered multilayer coating of SiO_2 and a CrZr alloy was deposited directly on top of a hardcoated polycarbonate substrate. By optimising the deposition conditions of the SiO_2 layer and the zirconium content within the alloy, a highly durable plastic mirror was achieved, which met automotive glass mirror specifications.

INTRODUCTION

The automotive industry has embraced plastic as its preferred engineering material in many components. The typical mass of plastic in today's car has reached 200 kg, up from only 10 kg in the 1960s [1]. Typically, where transparency and high durability is required, glass still has dominance, i.e. windscreens. However, the industry has successfully switched from glass to plastic in the construction of car headlights and taillights. This transition has allowed design freedom, and seamless integration of the headlight into the styling of the whole car. This transition has been driven by safety, weight reduction, enhanced functionality, material development, and modification to the design rules. A critical technological step was the development of highly durable and abrasion resistant hardcoatings, which impart the plastic with 'glass-like' properties [2]. These coatings were introduced into the ophthalmic industry during the 1970s [3] and transferred to the automotive industry in the 1980s [4, 5]. The coatings reduce UV degradation and allow the headlight to stand up to the harsh environment the automobile must endure. Over the past 100 years the headlight has transformed from an oil burning lantern to a stylised and fully integrated module at the front end of the vehicle.

One application which to date, has not undergone this transition is the rearview mirror, in particular the exterior mirror (wing mirror). In the case of mirrors, a glass substrate is highly scratch resistant, cheap and easy to metallise. However, it suffers from being dense, it is hard to form complex shapes with high accuracy (convex mirrors) and is prone to shatter in the case of an accident. Whereas, a plastic substrate, for example polycarbonate, is virtually shatter proof, can be injection moulded quickly to high accuracy and can offer a higher level of design freedom. The accuracy of the final shape of the injection moulded part is important as can result in a smaller mirror, as it can safely achieve the field of view required within the tolerances of the manufacturing process [6]. The injection moulding process can also be used to integrate clipping features to the rear of the mirror, to enable easy assembly and reduce the number of parts in the mirror assembly. The advantages of plastic over glass make it very appealing to the automotive industry and this is fuelling development. Attempts have been made to develop a coated, plastic automotive mirror by Venture-source, VTEC Mirror Systems LLC, Ficocipa SAS, Specchidea s.r.l. and Saudi Basic Industries Corporation (SABIC) [7]. However, none have been taken up by original equipment manufacturers (OEM). Durability and cosmetic issues have prevented any wide spread use [7].

Manufacturers offer both first surface glass mirror and second surface glass mirror. A first surface mirror has the reflective surface on the front of the glass substrate. A second surface mirror has the reflective surface on the back of the glass substrate, the first optical surface is then glass. Optically, the first surface is superior in performance, as the second surface

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mirror can display double images which eminent from the first optical surface (glass) and the second mirror surface. At night the double image can be especially distracting to a driver [8]. When considering the performance of these mirrors in durability tests, the first surface mirror is inferior to the second surface mirror. The location of the metal layer on the outer most surface leaves it exposed to the surrounding environment and makes it susceptible to degradation, most notable are fine scratches due to cleaning. The performance of both first and second surface glass mirrors has become accepted as the benchmark for alternatives to match.

This study reports of the development of a nano-engineered first surface mirror deposited on a polycarbonate substrate which matches first surface glass mirror performance. It combines previously published work [13, 16, 23, 24] into a coherent document detailing the important characteristics achieved and how they were brought together to deliver an automotive ready plastic rearview mirror. Conventionally, a metal layer would be deposited directly onto the polycarbonate substrate and then overcoated with a transparent protective layer. We report on the limitations of this approach and describe a more robust coating design, in which the layer orders are reversed. The polycarbonate substrate is hardcoated and then a sputtered multilayer of SiO_2 and CrZr alloy are deposited, such that a dense, impermeable system is achieved. We thus report on the optimisation of the multilayer system and the performance of the coating in corrosive tests. Finally, the development of a chrome zirconium alloy to give a neutral, scratch resistant mirror is described.

MATERIALS AND METHODS

The samples were manufactured by DC magnetron sputtering onto epoxy resin (PHC587B, Momentive GmbH, Germany) coated polycarbonate hardcoat-substrates. SiO_2 was deposited from high purity silicon (300 x 127 mm) target. Depositions were carried out under an argon / oxygen atmosphere in a custom built sputter system. Power was supplied through two Advanced Energy-MDX2.5 units (~ 2.4 kW), connected in series with an Advanced Energy-Sparcle providing additional arc suppression. SiO_2 deposition was carried out whilst the target was in a poisoned mode. The substrates were positioned on a grounded plate at a distance of 120 mm under the target, rotating at a speed of 20 rpm. The deposition pressure in the chamber was varied between about 0.2 to 0.6 Pa by variations in argon flow (12 to 30 sccm). The flow rate of argon to oxygen was kept at a constant ratio of 2 (oxygen flow was varied between 6 and 15 sccm). The substrate was heated via an IR lamp with thermocouple control during pump down. Substrate temperatures were measured by a tinytag temperature logger from Gemini Data Loggers with a pt100 thin film thermister located on the front of a plastic witness sample, temperature was varied between 55°C and 130°C. The subsequent reflective layer was deposited via sputter magnetron in the same chamber without venting. A large rectangular sputter magnetron (300 x 127 mm) with chrome target (~1 kW) under an argon and nitrogen atmosphere was used to deposit CrN_x. For the Cr alloy coatings an additional sputter magnetron (76 mm dia.) (25 to 200 W), with high purity targets of either Zr, Co, W, Ti and Mo was used simultaneously to co-deposit the alloy.

Performance based tests

First surface glass mirrors (Flabeg Holding GmbH, Germany) were chosen as a control, thirty three mirrors were split, three per test, across all of the eleven performance test (see below for test details). Thirty three plastic mirrors were tested in a similar protocol. In general, the integrity of the coating was quantified by comparing optical reflection before and after the test, visual assessment of any deterioration or delamination and the measurement of adhesion loss through an adhesive tape test (ASTM 3359) using 3M Scotch #8981 tape, (pull off force to steel 77 Nm/100 mm). Coatings are deemed to have passed a test if on completion there was no change in reflection greater than 1%, there were no visual defects and there was no loss in adhesion.

The corrosion resistance of the film was determined by analysis after being subjected to the salt spray test (ASTM B117). In this test the coating is subjected to a salt spray (fog) environment for extended periods of time (up to 1000 hrs) at an elevated temperature (40ºC), with the integrity of the coating tested during this period. The thermal shock test as per Ford BI 107 05:2009 tests the coatings ability to withstand temperature cycling from -40°C for 30 mins to +85°C for 30 mins, with a transition time of 30 secs, and repeated for 200 cycles. Solvent resistance was tested by exposing the coating for 10 minutes to solutions of KOH (30 %wt), HCL 10 %wt, chloroform, acetone, Diesel fuel per DIN EN 590, petroleum fuel per DIN 51604 B DIN fuel A. Evaluation of the performance of the coatings is by visual assessment and reflectivity measurements. A coating is deemed to have passed these tests if on completion there is no delamination, crazing or change in reflection greater than 1%.

Abrasion resistance was tested using the Bayer test (ASTM F735) which consists of exposing the samples to 500g ± 1g of Aluminium Zirconium Oxide (Alundum) of grid size 12 (ANSI B74-4 and B74-19) as the abrasive material in a tray which is oscillated for 300 revolutions. Reflected haze, before and after of an uncoated polycarbonate control and the sample is used to calculate the bayer ratio [9]. Water resistance was tested via two standard test methods, firstly in high humidity as per DIN EN ISO 6270-2 (500 hrs @95 %RH) and secondly, via immersion in warm water as per DIN 50017 (320 hrs @ 40°C). Resistance to deterioration at high temperatures was tested via the dry heat as per IEC 68-2-2 (1974) - 1 hour at 110°C. Accelerated weathering was performed with an atlas Ci4000 weatherometer, with quartz inner and outer filters set to follow SAE J1960 exposure protocol, testing was performed until the sample accumulated at total of ~3960 kJ/m^2, which is roughly equivalent to ~ 3 yr simulated UV exposure. Impact test was carried out under UN/ECE R46 Rear-view Mirrors, 0.5 kg dropped from 20 cm with a 38 mm diam. impact head at room temperature.

RESULTS AND DISCUSSION

Coating design

Conventionally, a metal layer of a plastic mirror has been positioned underneath a protective hardcoating. This placement was to ensure maximum protection from corrosive agents and abrasion damage. However, it has been found that the metal layer disrupts the adhesion mechanism between the polycarbonate and the hardcoating resin [7], as most resin based hardcoatings are designed to partially dissolve the polycarbonate and form an interface with high adhesion [10]. Any disruption of this mechanism can lead to adhesion issues resulting in delamination of the overlying coatings. Additionally, the presence of a thin optically transparent layer positioned on top of a reflective metal layer produces optical interference yielding patterned fringes that are cosmetically undesirable. One alternative is to use a thick transparent layer, commonly known as a clear coat, to supress interference fringes [4]. However, it has been found that coatings of this thickness (> 20 µm) are susceptible to crazing or have low scratch resistance.

To overcome these limitations the hardcoating was located directly on the polycarbonate. This then forms a PC-hardcoat interface, as seen in the car headlight example mentioned previously. This system has proven to exhibit excellent adhesion and to be robust through the full range of automotive durability and performance testing. However, this then requires the mirror layer to be deposited on top of the hardcoating and it effectively becoming the first layer of the system. As such, the metal layer must be inherently scratch resistant and corrosion resistant.

Following conventional coating design, as used in the ophthalmic industry [11], the initial layer in the multilayer coating system was ~ 130 nm of SiO_2. This layer acts to enhance the abrasion resistance of the hardcoating and forms a well adhered coating to the hardcoating. The polycarbonate – hardcoat-SiO_2 system forms a "glass-like" substrate for the subsequent deposition of the metal reflective layer.

Examination of the current automotive first surface glass mirrors can be instructive. These mirrors use chrome as the reflective layer. Chrome is inherently corrosion resistant, as it self passivates with a thin CrO layer [12], the level of reflectivity and colour are already accepted as industry standard and well exceeds the minimum 40% for an exterior wing mirror. Thus, chrome was also chosen as the reflective material for the plastic mirror.

The polycarbonate – hardcoat – reflective multilayer design overcomes the limitations previously described, Figure 1. That is, the mirror is on the very front, so no interference fringes are observed and the polycarbonate-hardcoat interface is maintained which results in a stable base. Additionally, an enhanced UV resistance is achieved, due to the presence of the metal layer on top of the susceptible plastic substrate. The metal layer transmits a negligible amount of UV light, significantly reducing the amount penetrating into the polycarbonate and causing any damage. Additionally, the rear of the plastic can be left uncoated, and thus free for added functionality. For example, the integration of mounting clips, such that the mirror can be directly mounted to the actuator motor mechanism or the direct application of a metal backing layer for defrost function.

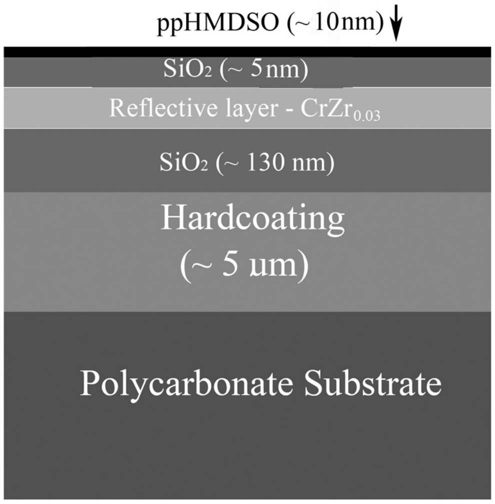

Figure 1: The final plastic mirror stack design.

Corrosion resistance

Corrosion resistance was found to be critical in the development of the multilayer thin film system [13]. Interestingly, it was not the metal layer that was found to be susceptible. During salt spray testing delamination of the sputtered layers from the underlying hardcoat was observed. Measurements with a profilometer confirmed the failure had occurred at or near the hardcoat – SiO_2 interface. It is known that SiO_2 is susceptible to hydrolysis [14] as such, it is proposed that the SiO_2 underwent corrosion leading to the delamination observed. XPS analysis showed correct stoichiometric ratio was obtained for deposition conditions, thus degradation due to sub-stoichiometric SiO_x was not believed to be responsible.

Experimentation with the deposition conditions during sputtering of the SiO_2 layer showed that the time to failure in the salt spray test could be extended when the coating was deposited under high temperature (130°C) and low pressure (0.2 Pa), see Figure 2.

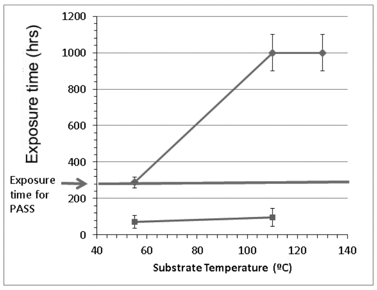

Figure 2: Effect of deposition conditions of SiO_2 (substrate temperature and low pressure (■), high pressure (◆)) on time to fail in salt spray corrosion test. Exposure time which is considered a pass is 288 hrs (dark horizonal line).

Direct evidence of the structure of the deposited SiO_2 layer was difficult to obtain, due to the insulating nature of SiO_2 electron microscopy produced no useable information [15]. As such, surface characterisation was achieved via AFM. It is known that surface roughness can be linked to the layers internal structure [16]. The interfacial area of the different SiO_2 coatings was quantified via AFM scans for SiO_2 deposited at high pressure / low temperature (fail) and low pressure/ high temperature (pass) condition. The rms roughness was determined for each condition and is presented in Table 1. In practice, AFM imaging of the neat SiO_2 was not possible due to capillary condensation occurring between the small radius AFM tip and the hydrophilic SiO_2 coating at relative humidity's down to 25 %. To suppress the capillary condensation, the samples were coated with a 5 nm Cr layer. It was observed that the coatings deposited at high pressure/ low temperature had a rough surface. The coatings deposited at low pressure / high temperature had a smooth surface. It is hypothesised that SiO_2 grown high pressure/ low temperature conditions have an open porous structure resulting in an increased surface roughness. Whereas, SiO_2 coatings deposited under low pressure / high temperature conditions have a highly dense structure and hence a smoother surface.

Table 1: RMS roughness values for the SiO_2/Cr layers deposited under different conditions.

	High Pressure / Low power	**Low Pressure / High Power**
RMS roughness 10 x 10 µm scale (nm)	2.3 ± 0.2	1.6 ± 0.1
RMS roughness 100 x 100 µm scale (nm)	2.7 ± 0.2	2.2 ± 0.2

It is further proposed, that the density of the SiO_2 layer affected the ingress of the electrolyte (NaCl). The high pressure/low temperature layer dissolved, resulting in the delamination of the multilayer mirror. Conversely, the low pressure/high temperature resisted penetration of the electrolyte and stopped the corrosion of the coating. Further pitting corrosion results can be found in ref [13].

Chrome Zirconium Alloy- Scratch resistant mirror

It was found that chromium alone did not display sufficient abrasion resistance when positioned as the upper most layer in the plastic mirror multi-layer system. Work was undertaken in developing an alloy with superior abrasion resistance whilst maintaining a neutral colour. The addition of a dopant material to the chrome was explored. The packing density of a materials atoms and their spatial arrangement can be altered by the addition of a dopant material during sputtering. This is known to produce harder or softer phases within the material. Much of this work involves the development of hard compound coatings, such as borides, carbides and nitrides [17-20] at high temperatures. It is known that CrN can be used to impart abrasion resistance to cutting tools [21, 22]. It is the crystal structure (Face Centred Cubic, FCC) that yields the high strength of the material. However, conventional processing techniques are at evaluated temperatures which are unsuitable for plastic substrates. In addition the colour is shifted to an unacceptable yellow/orange. Thus, alternative dopants were investigated, primarily transition metals to create alloys.

Thin film coatings of ~ 40 nm of chrome alloy were deposited by magnetron co-sputtering onto the polycarbonate – hardcoat – SiO_2 multilayer system, previously described. The alloy was generated from the multi-pass deposition of alternating angstrom thick layers from each respective target [23]. The co-sputtering generates thin film coatings of Cr doped with another metal (Zr, Mo, W, Ti or Co) where the atomic percentage of the dopant was varied between 1 % and 20 %. Dopants such as these have been shown to modify the structure of Cr based coatings by replacing Cr atoms within the Body Centred Cubic (BCC) crystal lattice [20]. This modification of the atomic structure of the BCC Cr coating was observed and quantified by measuring the lattice parameter of the crystal structure using electron diffraction. Further, it has been reported that alloys of Cr benefit from the corrosion resistance of chrome and its self passivating nature [12]. The incorporation of dopant and the resulting change in lattice parameter was observed to correlate with the macroscopic abrasion resistance. Depending on the class of dopant metal (be it BCC or hexagonal close packed, HCP) and the atomic concentration of that dopant, the degree of modification of the BCC Cr crystal lattice was controlled. Figure 3 shows the effect of dopant type when at the optimum concentration.

Figure 4 shows the effect on abrasion resistance for a range of atomic concentrations of Zr [16]. The Cr alloy with the optimum abrasion resistance (chromium zirconium at 3 %) was chosen for further evaluation.

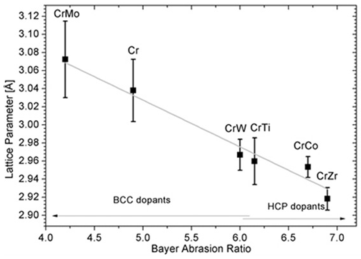

Figure 3: The relationship between the atomic structure (defined by Å) and the macroscopic mechanical properties (abrasion resistance). Note that the HCP dopants generally give greater reduction in the lattice parameter and greater resistance to abrasion compared to the BCC dopants. Reprinted from Surf. Coat. Technol., 206 (2012), K. Zuber, C. Hall, P. Murphy, D. Evans "Atomic structure studies of chrome alloy coatings and their abrasion resistance" with permission from Elsevier.

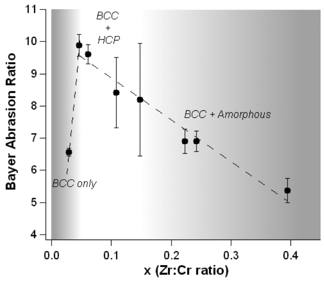

Figure 4: The relationship of zirconium concentration in Cr alloy and the abrasion resistance as measured by the Bayer test. Reprinted from Surf. Coat. Technol., 206 (2012), D. Evans, K. Zuber, P. Murphy "Ultrathin films of co-sputtered CrZrx alloys on polymeric substrates" with permission from Elsevier.

Automotive based performance tests

Finally a capping layer system was deposited to enhance scratch resistance and achieve a hydrophobic surface to enhance the cleanability of the mirror. The capping layer system consisted of a SiO$_2$ layer approximately 5 nm and a siloxane layer deposited via rf PECVD at 40kHz from the precursor hexamethyldisiloxane (HMDSO) approximately 10 nm. It was found that the capping layer system reduced the surface roughness and friction which resulted in an increase in abrasion resistance [24].

The optimised plastic mirror multi-layer system was subjected to a range of automotive based performance tests, Table 2. For comparison purposes a control glass mirror was put through the same tests at the same time. For all tests the plastic mirror met or exceeded the glass mirror performance. Of particular note is the impact resistance of the plastic mirror, under testing the substrate maintained its shape and functionality, the glass mirror shattered and loss functionality.

Whilst the rigid substrate of the glass has provided an excellent based for the deposition of a reflective layer, this system has proven very durable and has been in use for many years. Only by careful material selection and deposition has a plastic version been possible. The main challenge that needed to be surmounted was the soft compliant nature of the substrate. The plastic mirror system, as described above, has proceeded to commercialisation.

CONCLUSION

Highly durable plastic mirrors have been developed which meet automotive specification for exterior wing mirrors. The correct design of the multi-layer system was critical in achieving a highly adherent and cosmetically acceptable mirror. The multi-layer system developed consisted of a polycarbonate substrate – hardcoat – SiO$_2$ – CrZr$_{0.03}$ reflective layer. It was found that a dense, stable SiO$_2$ layer was required to avoid hydrolysis. The development of chrome zirconium alloy modified the atomic structure, which lead to an increase in the measured abrasion resistance. With the addition of a capping layer, the system was benchmarked against a standard glass mirror. The plastic mirror system was found to match or exceed the first surface glass mirror.

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Table 2: Automotive based performance test results of a first surface glass mirror and a plastic mirror as per Figure 1.

	First surface glass mirror	**Plastic mirror**
Optical Reflectivity (legal requirement > 40 %)	63 %	55 %
Abrasion (Bayer Test) Abrasion ratio	12 ± 2	10 ± 2
Abrasion (Steelwool test)	4 / 5	4 / 5
Adhesion	5 / 5	5 / 5
Environmental – accelerated weathering	No crazing / delamination / yellowing	No crazing / delamination / yellowing
Thermal Shock	No crazing / delamination	No crazing / delamination
Solvent Resistance	No residual marking	No residual marking
Humidity	No crazing / delamination	No crazing / delamination
Immersion	No crazing / delamination	No crazing / delamination
Corrosion	> 1000 hours	> 1000 hours
Dry heat	No crazing / delamination	No crazing / delamination
Impact Test	Substrate cracked	Crazing of coating

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