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Artificial aging of tin amalgam mirrors: a preliminary study of alteration compounds and kinetics.

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Abstract

This preliminary study aims to investigate for the first time the kinetics of degradation of tin amalgam mirrors reflective layer. For this purpose some specimens of tin amalgam mirrors have been created, characterized and then subjected to artificial aging. The monitoring of the degradation was done by different techniques such as XRD, SEM and UV-VIS Reflectance Spectroscopy. They allowed to evaluate the progressive color and morphology changes of the amalgam layer, but no expected degradation compounds of amalgam, such as cassiterite and romarkite, were detected. The possible mechanisms underlying the experimental results and further experimental procedures and tools are discussed.

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Keywords: Mirror; Tin amalgam; Artificial aging; SEM; XRD; UV-VIS Reflectance Spectroscopy; mercury;

1. Introduction

For the first time in this work the kinetics of degradation of tin amalgam mirrors reflective layers have been investigated. In amalgam mirror a film of tin amalgam is adhered by pressure to a glass sheet. This ancient technique was probably discovered in the fourteenth century in Germany and then developed in Venice in the sixteenth century. Although the methods of production of amalgam mirrors were jealously guarded by the venetians glassmakers, the technique quickly became widespread all over Europe. This method has been the only one used for the mirrors production until the nineteenth century, when the method of silvering was invented. Tin

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amalgam is a binary alloy of tin and mercury. The investigations performed to date have shown that tin amalgam is formed from two different phases (Fig. 1a), with 25 % wt. of total mercury content: a solid phase rich in tin, and a mercury-rich liquid phase saturated with tin. The solid phase is composed by mercury (~ 20 % wt) and tin (~ 80 % wt), while the surrounding liquid phase consists of mercury (95 - 100 % wt) and tin (0 - 5% wt).

The amalgam alteration processes produce mercury evaporation and a general growth of the solid phase crystal size. In addition, tin dioxide (cassiterite - SnO_2) and monoxide (romarkite - SnO) are formed [1-8]. These cited studies allowed a good characterization of both amalgam and its degradation products. However only one paper concerning a first approach on the degradation mechanisms of the amalgam has already been published by Hadsund [1].

For this purpose some specimens of tin amalgam mirrors to be artificially aged were created and studied in the present work. The monitoring of the degradation was done by different techniques such as XRD, SEM and UV-VIS Reflectance Spectroscopy. They are useful to evaluate both the progressive color change of the amalgam layer and the formation of degradation compounds of amalgam as well as the possible correlations between these phenomena.

2. Materials and Methods

2.1. Preparing tin amalgam mirror

A tin amalgam mirror to be submitted on artificial aging has been produced on the basis of the recipes described by Hadsund [1] and Franceschini [9].

As suggested by Hadsund [1], a tin sheet of 14x14 cm size, 0.127 mm thickness, 99.9% purity was used for the preparation of the tin amalgam film. He fabricated different mirrors using different thickness tin foils of 0.1, 0.03, and 0,013 mm: the results show that the thick 0,1 mm foil ensured the best results.

In this work mercury was 99,9% pure and the glass sheet was a float glass smoothed, abraded and cleaned with cerium oxide. According to the Franceschini's recipe [9], the tin foil was laid on a marble floor.

The area of the tin foil was then bordered by four little glass sheets and mercury was poured onto the tin foil. The mercury layer was about 2-3 mm thickness [Fig. 1 (b)]: the amount necessary to completely cover the tin foil was approximately 200 ml.

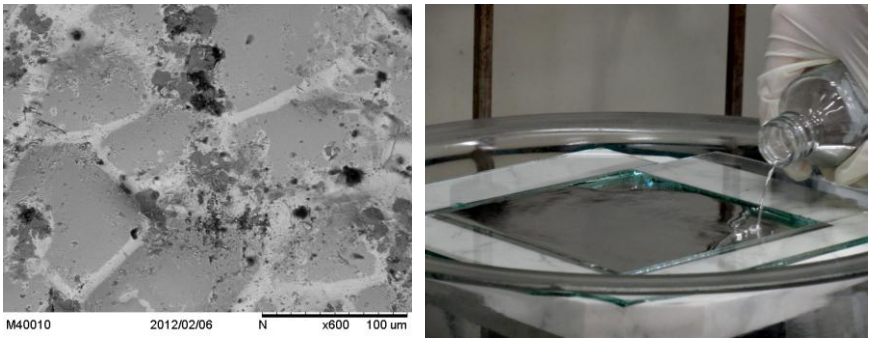

Fig. 1. (a) SEM image (600x) of a tin amalgam layer area; (b) Preparation of the tin amalgam mirror.

The glass sheet was superimposed by sliding over the mercury layer to create a homogeneous adhesion on the whole glass surface. The glass sheet was left few minutes in this position in order to eliminate any air bubbles formed at the interface glass-mercury. The mirror was then left to dry for about 15 days, first in a horizontal and then in an oblique position to remove the mercury excess.

The mirror was then placed in a vertical position for 20 days, until any mercury dripping disappeared.

The finished mirror (hereafter sample MM) was cleaned, photographed and inspected by stereomicroscope and Scanning Electron Microscope.

2.2. Artificial aging

The artificial aging was performed by a ASCON-MIU Y 3/88.04 climatic chamber. It was performed on mirror fragments of about 4 cm diameter to allow XRD and colorimetric analyses. An ancient amalgam mirror well-preserved (sample M4) and an amalgam mirror granted by Steffen Noack of SpiegelArt (sample MN) were used for artificial aging, in addition to the MM sample.

Before the artificial aging, both amalgam layer and glass of these three mirrors were photographed and characterized using different analytical techniques (SEM, XRD, and UV-VIS Reflectance Spectroscopy), for comparison purpose with the results obtained after the aging.

During the period of aging in the climatic chamber the samples were periodically removed, photographed and investigated by SEM, colorimetric analysis, and XRD to evaluate the progression of the degradation.

In order to establish the temperature and humidity conditions for aging, some preliminary tests were performed. In his study, Hadsund [1] aged some samples of self made amalgam mirror at 20° and 50° C for a month. He obtained only a growth of the solid phase crystal size without formation of tin oxidation compounds expected from natural weathering.

In order to assess the conditions of temperature and humidity and the time required to get a first visual change of the samples appearance, some fragments of MN sample were undergone to the following conditions:

- 48 hours at 60° C and 60 % R.H..The sample didn't show any change by either naked eye or stereomicroscope inspection.
- 120 hours at 80° C and 80 % R.H. The sample appeared slightly yellowed and with some opalescence on the edges of film amalgam.
- 4 hours at 150° C and 10 % R.H. The sample showed a blue layer above a metal layer. The XRD analysis showed the presence of amalgam and romarkite (SnO) but the SEM images show the presence of a phase very different from both the initial amalgam and that of ancient mirrors.

As a consequence artificial aging at 90° C and at 90% R.H. for about 1000 hours was carried out.

2.3. Monitoring during artificial aging

The trend of the aging process has been evaluated by photographic survey (orthogonal and details), SEM investigation, UV-VIS Reflectance Spectroscopy and X-ray Diffraction (XRD).

The photographic, colorimetric and XRD analyses were performed every 2/3 days for 40 days (960 hours).

Every colorimetric analysis was carried out on a previously marked area of each sample. This allowed to assess the color change of the sample in a limited region: in fact the data about the different areas of a sample may provide discordant information due to the presence of local in-homogeneities which influence the chromaticity. The measurements were taken by a integrating sphere spectrophotometer (d-MINOLTA CM-2600) in the wavelength range 360 - 740 nm, 10° angle and resolution of 10 nm. The investigated area had a diameter of 0.8 cm (MAV mode) and the measurements were carried out in SCI mode for three times for each sample within the delimited area, calculating the average of the resulting values. The parameters L*, a*, b*, λ_D (dominant wavelength), h (hue) and C* (color saturation) were plotted vs. artificial aging time.

The XRD analyses were performed using a X ray diffractometer PANALYTICAL X'PERT PRO MPD equipped with a high sensibility detector PIXCELL. The qualitative identification of phases was carried out by the X'PERT SCORE PLUS software using the ICDD database (International Centre for Diffraction Data).

The SEM analysis was performed using a Scanning Electron Microscope JEOL JSM 5900. The samples were fixed by a carbon double-sided tape on a aluminum sample holder and metallized under vacuum with graphite to ensure a good conductivity.

3. Results and Discussion

The MN, MM and M4 samples artificial aging monitoring results were reported in the following sections.

3.1. Opical monitoring

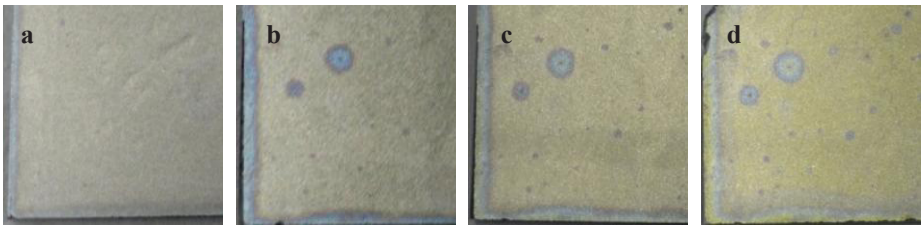

Fig. 2. Pictures of the MN sample at different aging time values at 90° C and 90% H.R.: (a) before the artificial aging; (b) after 240 hours of artificial aging (c) after 500 hours; (d) after 960 hours.

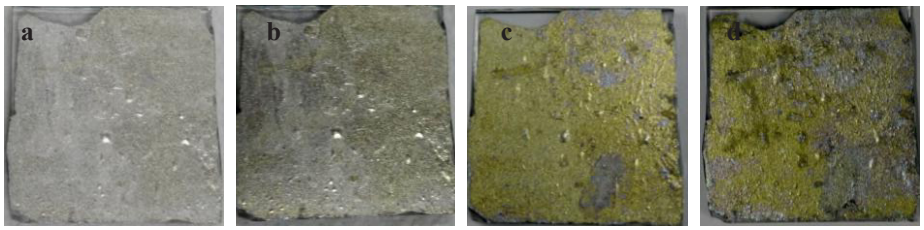

Fig. 3. Pictures of the MM sample at different aging time values at 90° C and 90% H.R.: (a) before the artificial aging; (b) after 240 hours of artificial aging (c) after 500 hours; (d) after 960 hours.

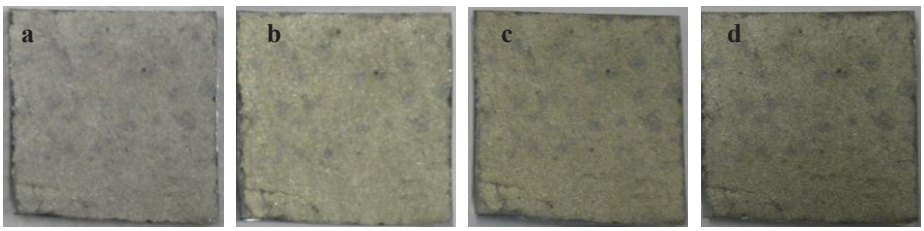

Fig. 4. Pictures of the M4 sample at different aging time values at 90° C and 90% H.R.: (a) before the artificial aging; (b) after 240 hours of artificial aging (c) after 500 hours; (d) after 960 hours.

The visual inspection of the photographic pictures of MM, MN and M4 samples at different times of artificial aging (Figs. 2, 3 and 4) showed for all the samples a gradual color change of the reflective layer, from silvery-gray to yellow. In particular, this color change was very obvious in the samples MM and MN, and much less evident for the sample M4, already naturally aged. Moreover the samples MM and MN showed the formation of iridescent blue-purple patches. These stains, irregularly shaped on the sample MM and concentric on the sample

MN, grew along the time on the sample MM up to cover almost half of the sample surface after 960 hours. On the contrary, those formed on the sample MN grew up to a maximum in the first 240 hours and then stopped.

In addition to the internal concentric iridescent staining, the sample MN showed the same type of color change also on all the edges of the amalgam layer.

3.2. SEM investigation

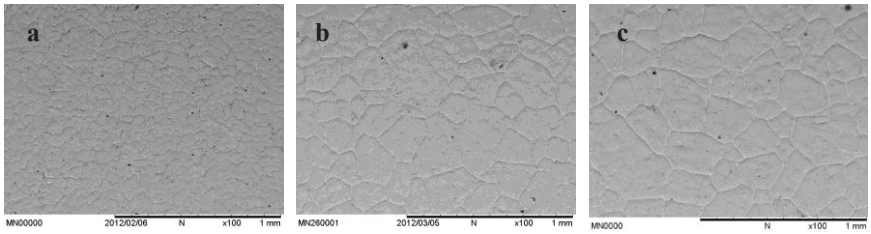

Fig. 5. SEM image (100 x) of the MN sample at different aging time values at 90° C and 90% H.R.: (a) before the artificial aging; (b) after 500 hours of artificial aging (c) after 960 hours.

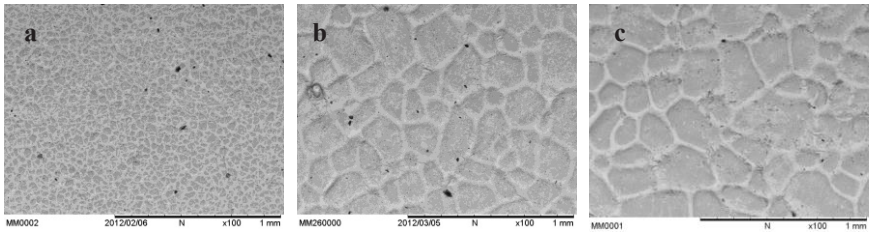

Fig. 6. SEM image (100 x) of the MM sample in different aging times values at 90° C and 90% H.R.: (a) before the artificial aging; (b) after 500 hours of artificial aging (c) after 960 hours.

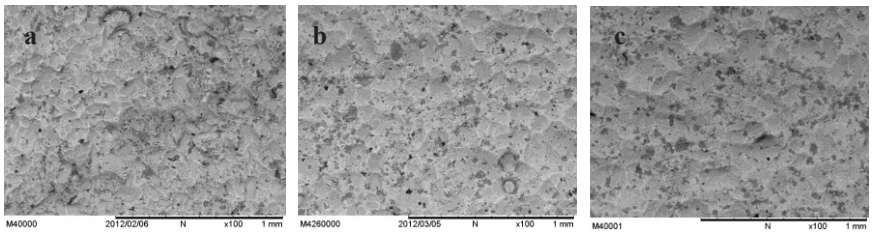

Fig. 7. SEM image (100 x) of the M4 sample in different aging times values at 90° C and 90% H.R.: (a) before the artificial aging; (b) after 500 hours of artificial aging (c) after 960 hours.

SEM analysis allowed to note the increase in time of the magnitude of the clusters of the amalgam solid phase (Figs. 5, 6 and 7). As also observed by Hadsund [1], over time and at high temperatures the clusters of the solid phase tend to increase their size, agglomerating to each other. The cluster size increase is much more evident in MM and MN samples, ad less pronounced in the M4 sample, already naturally aged. This increase in size may be due to loss of liquid phase by evaporation. The increase of magnitude of solid phase clusters allows the adhesion of amalgam to the glass in spite of the loss of mercury. By measuring the mean linear size of the amalgam clusters, it was possible to evaluate the asymptotic trend of their growth with time (Fig. 8).

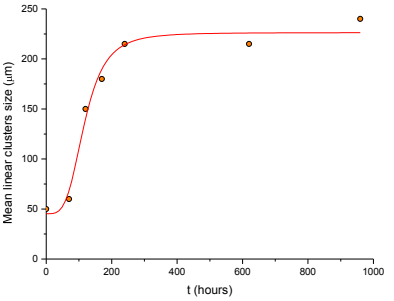

Fig. 8. Growth of the mean linear size of the solid phase clusters in time during the artificial aging (MN sample)

3.3. UV-VIS Reflectance Spectroscopy

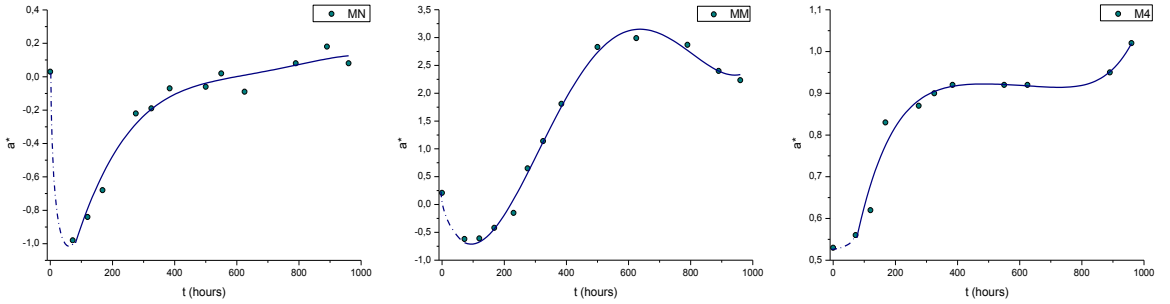

Fig. 9. Variation of the colorimetric parameter a* during the artificial aging.

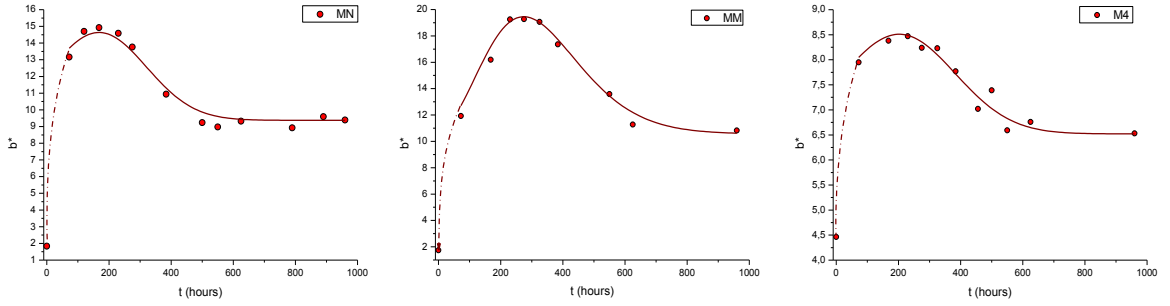

Fig. 10. Variation of the colorimetric parameter b* during the artificial aging.

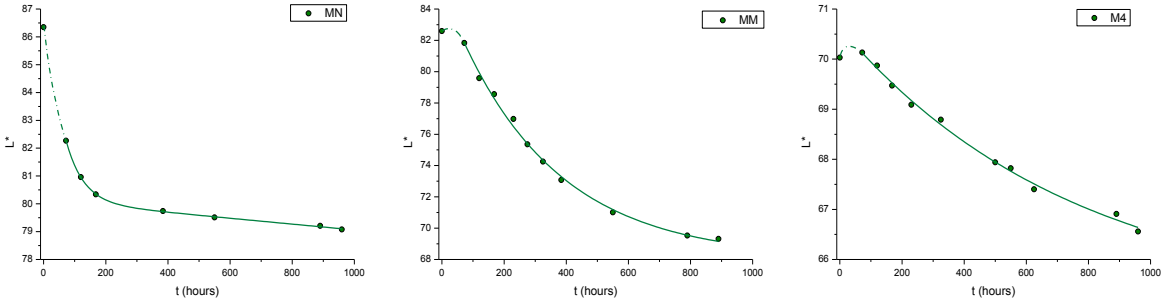

Fig. 11. Variation of the colorimetric parameter L* during the artificial aging.

The colorimetric analyses evidenced a general decrease of brightness L* parameter during the aging period (Fig. 11). This decrease is especially pronounced for the MM and MN samples, and rather low for the M4 sample. This different behaviors could be explained by the fact that the ancient mirror sample M4, has already undergone to brightness changes over time: in fact the initial value of L* of M4 sample was lower than the initial values of L* in MN and MM samples.

The gradual yellowing of the samples is indicated by the colorimetric parameter b*. It is possible to note how, for all the three samples b* increases to a maximum value and then asymptotically decreases, following a double exponential curve (Fig. 10). The asymptotic values are higher than the initial ones, but lower than the maximum value. This not monotone trend doesn't be noticeable by the simple visual inspection.

The variation of the a* parameter (Fig. 9) shows different trends for every samples. Although this may be due to different behaviors of the samples, the variation of a* is much lower than the b* one and a* variation results practically negligible.

3.4. X-Ray Diffraction

The XRD analysis detected for all the samples and any aging time the only presence of tin amalgam. However, differences in the reciprocal intensities of the diffraction peaks were observed between the different samples and stages of aging. This is probably due to a preferential orientation of growth of the solid phase crystals during the progressive re-crystallization of tin amalgam [1].

It is worthnoting also a general increase of the diffraction signal with aging time.

Despite the conditions of artificial aging proved to be not adequate to the simulation of natural weathering processes, because X-ray diffraction analysis didn't detect the formation of degradation compounds (such as romarkite and cassiterite), the amalgam has undergone to some changes.

The yellow layer and the blue-purple iridescent stains formed on the surface of the tin amalgam could consist in a tin oxidation layer. This layer, very thin and easily removable, could not be detected by SEM analysis and X-ray Diffraction. Therefore, to test this hypothesis it would be necessary a more detailed study, with an extension beyond 40 days of the artificial aging and the use of further investigation techniques, such as GIXRD or EPMA-WDS.

Furthermore, the yellowing of the superficial layer and the signal diffraction intensity increase could be due to the increase of the solid phase clusters size. If the amalgam surface is affected by modifications, the visible light could be differently reflected and cause the appearance of different colors. Similarly, the size increase of the clusters of the crystalline phase could produce the diffraction signal raising.

4. Conclusions

This work allowed to face the study of ancient techniques of mirror production and the aging effects through the creation of a tin amalgam mirror sample.

The artificial aging, despite the used conditions proved to be not adequate to reproduce the weathering processes, allowed to detect that amalgam has undergone to some changes.

These changes can be caused by some alteration processes different from the natural ones or by formation of a thin layer of oxidation not detectable through XRD analysis.

A more detailed study and an extension beyond 40 days of the artificial aging are therefore desirable in order to understand the adequate conditions for the artificial aging and for the study of the kinetics processes of the formation of tin amalgam natural decay compounds.

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