**SiO₂ as gas barrier and nano holes in SiO₂ flakes**

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**Abstract.** Sublimation of SiO is used to protect PVD aluminium flakes from water corrosion and to generate highly porous SiO₂ flakes with holes in the nanometer range. SiOₓ/Al/SiOₓ sandwiches were made as well as Ag loaded porous SiO₂ as antimicrobial filler.

1. **Introduction**
Popular liquid metal colors require the use of mirror-like aluminum pigment manufactured in a high vacuum process (hereafter PVD). Best optical reflectivities are achieved with flake thicknesses around 40 nanometers [1]. The reaction in water of neat Al flakes is a well know issue and various surface treatments have been proposed [2], [3]. SiO₂ as gas barrier against Al corrosion has been discussed in [4] and is known for a long time [5].

A high vacuum process to sandwich PVD Al between two SiO₂ layers made by SiO sublimation has been investigated in an attempt to protect PVD Al in water environment. A similar high vacuum process lead to highly porous SiO₂ flakes.

2. **Experimental**
A high vacuum chamber is equipped with 4 evaporation sources (Joule heating) and 4 thickness measurement units. Al is evaporated by the conventional flash method. SiO preparation and sublimation are described in [6].

A water soluble release layer is first evaporated on a continuous carrier; Al and SiO are then evaporated, respectively sublimed, in desired order on the release layer. The carrier is removed from the vacuum chamber, the water soluble release layer is dissolved and the inorganic flakes are collected. A well known release layer is NaCl [7]. Water soluble organic release layers can also be employed, among them penthaerythritol [8]. Vapor pressure of SiO [9] and NaCl [10] are high enough to allow high evaporation rates at moderate temperatures.

The optical reflectivity has been measured with a micro photo spectrometer from J&M. The spot size is 5 microns.

3. **Results**

3.1. SiOₓ protected Al flakes
The sandwich structure of a particle of SiOₓ/Al/SiOₓ (x~1.8 to 2) is shown in Figure 1. The aluminum layer of 30 to 50 nm is situated between two homogenous SiOₓ layers of 10 to 20 nm each. The SiOₓ layers are acting as gas barriers to protect the Al from further degradation by water for example. The particle side is bare, unprotected, aluminum but represents a small portion of the whole surface. No further surface modification was made on the present sample. The effect of the difference in thermal expansion between SiOₓ and Al has not been investigated.
3.1.1. Influence of the release layer on the bare aluminum reflectivity

The thickness and evaporation conditions of the NaCl release layer affect the optical reflectivity of the particles, even if the evaporation conditions are appropriate for aluminum alone.

At constant thickness of the release layer, the Al reflectivity is becoming light yellow when the pressure increases. A similar effect is observed at constant vacuum and increasing thickness of the release layer. Both observations are now fully understood but go beyond the scope of the present paper. All samples were then made with a 50 nm thick release layer of NaCl under a vacuum better than $10^{-4}$ mbar.

3.1.2. Effect of the SiO$_x$ layer on the optical properties of SiO$_x$/Al/SiO$_x$ flakes

SiO$_x$ coated Al in air features a slightly lower reflectivity than the bare aluminum, as shown in Figure 2, where each curve is the average of 5 different evaporation batches. The SiO$_x$ coated Al batches were heated in air at 200°C for 1 hour in an attempt to fully oxidise the SiO$_x$ layers.

![Figure 2. Reflectivity of bare aluminum flakes (--) and heated SiO$_x$ protected Al flakes (—).](image)
The index of refraction of SiO\textsubscript{x}, x\approx1.8 is very close to the one of SiO\textsubscript{2} [11] and the loss in reflectivity cannot arise only from the difference in refraction index between SiO\textsubscript{x} and air. More detailed investigations are required to understand this slight alteration of the reflectivity.

### 3.1.3. Water resistance of SiO\textsubscript{x}/Al/SiO\textsubscript{x} flakes

Both protected and unprotected aluminum feature hydrogen generation in water set at pH of 8.0. The volume of hydrogen generated by protected aluminium flakes and unprotected ball milled aluminum is reported in Figure 3. The silica based protecting layer postponed the start of hydrogen generation by about 24 hours. The total amount of evolved hydrogen corresponds to the full conversion of metal Al in Al hydroxide. Optimisations are still required.

![Figure 3. Amount of generated hydrogen in protected (\(\triangle\)) an unprotected aluminium (■) by aqueous corrosion medium (2\% Akropal N100). The gas volume is standardized on the Al content.](image)

3.2. Porous SiO\textsubscript{x} flakes

The co evaporation of the release layer and SiO allows making highly porous SiO\textsubscript{x} flakes, as shown in Figure 4 [12].
Figure 4. SEM micrograph of porous SiO$_x$ flake. The estimated pore density is $3 \times 10^6$ cm$^{-2}$. The rms-roughness is between 3 and 20 nm. Pore sizes according to BET measurements are between 2 and 5 nm with a maximum at 3 nm.

The porosity depends on the ratio NaCl/SiO$_x$ and can be adjusted from 0 to close to 70%. The “pore” backbone consists in a percolating network of channels with a diameter of a couple nanometers. The flake thickness is 50 nm or more and its specific surface ranges from 500 to 900 m$^2$/g. Such porous substrates can be loaded with metallic silver particles. The handling of large flakes with nano holes filled with silver is easier than that of powder of silver nano particles [13].

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