Final Report:

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"Deposition and Characterization of Thin Films on Metallic Substrates"

Principal Investigator
Dr. Jorge E. Gatica, Associate Professor

Affiliation
Department of Chemical & Biomedical Engineering
Cleveland State University
1960 East 24th Street – SH455
Phone: (216) 523-7274 / FAX: (216) 687-9220
E-mail: j.gatica@csuohio.edu

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Project Objectives

The main objective of this research was to develop a testing protocol that would ensure systematic assessment of the film effectiveness to improve adhesion properties. The protocol was applied to films produced with precursors based on iron additives. Precursors based on magnesium additives were also investigated.

Methodology Used

The CVD experiments were performed in a Thermolyne™ 21100 Tube Furnace using a mullite tube 0.9-inch ID. A cast iron block (3.82 x 0.86 x 0.25-inch^3) with a machined 0.8-ml cylindrical well was used as a solution and sample holder. The well was filled with a solution and an aluminum coupon is placed on the flat stage of the holder. Once ready, the sample holder is slid half way into the furnace. Pure aluminum metal (+ 99.99%) and aluminum alloy 3004, both 0.5-mm thick, were used in this study. The furnace was then programmed for controlled heating from room temperature to 400 °C at 5 °C/min. In addition to the temperature controller used with the furnace, the sample holder was fitted with a copper-constantan thermocouple. Exploratory studies revealed the following issues: (i) the CVD process occurred for temperatures within the range of 300 to 400 °C; therefore, the experiment was considered complete when the holder reached 400 °C, and (ii) successful conversion coatings were visibly yellow.

The CVD method utilized solutions of aryl phosphate esters and transition metal organic (organometallic) additives. In this work the effect of magnesium is reported. These additives are typically supplied as highly hygroscopic powders and have solubility limits in aryl phosphate esters. Precursors were prepared following a protocol developed in a previous research (NASA

Grant NCC3-971). FTIR of the precursors was used to assess chemical interactions between the additive and the phosphate esters. Chemical kinetics for these precursors were studies using calorimetric analyses.

Early attempts to characterize the film thickness with a Scanning Electron Microscope (SEM) were unsuccessful. The films were too thin to show a distinctive structure by SEM. The films were then analyzed using X-ray Photoelectron Spectroscopy (XPS). FTIR measurements using a reflective FTIR attachment (grazing-angle FTIR measurements) were used in this research. Adhesion enhancement properties of the films were assessed using two methods: (i) the standard ASTM tape-test method, and (ii) a mechanical testing unit (Sebastian IV Adhesion Tester, donated by NASA Glenn to CSU in Summer 2004). Results from FTIR and adhesion analyses are reported below for coatings produced with iron-based precursors.

Results Obtained

Kinetic Characterization

Film deposition experiments within a hermetically sealed DSC pan were to estimate the kinetic parameters of the reactions, namely activation energy (E_a), pre-exponential factor (k_o), and reaction order (n).

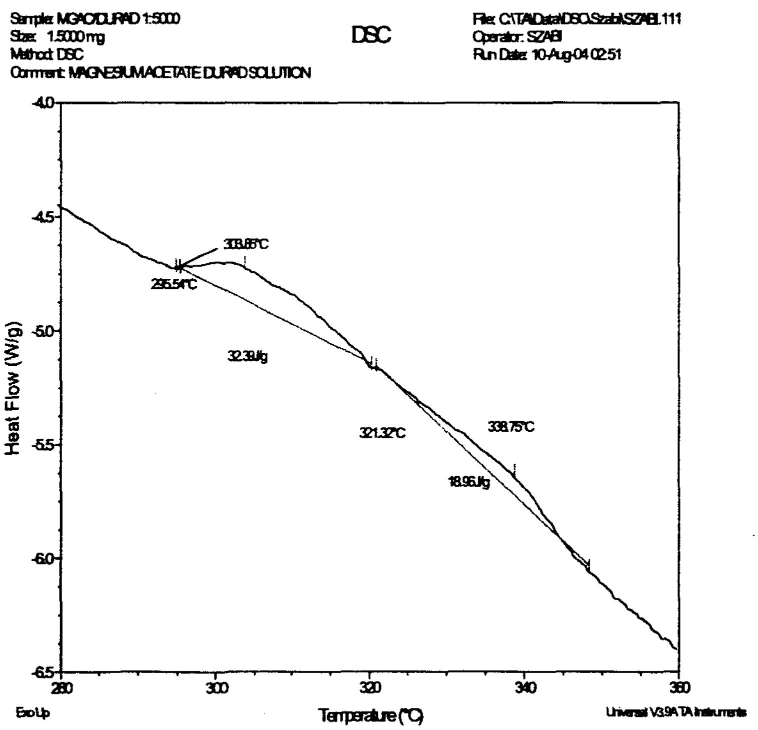

Figure 1: DSC output of Heat Flow vs. Temperature

Using Differential Scanning Calorimetry (DSC), we were able to identify the presence of two exothermic reactions occurring at clearly identifiable different thermal ranges. A typical DSC experiment is shown in Fig. 1. The data was analyzed using the Borchardt and Daniels' method, and preliminary kinetic characterization was possible.

Tape Adhesion Testing

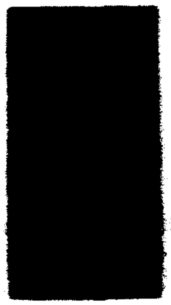

Figure 2

Adhesion tests were performed using the standard testing method ASTM D3359-02. Small coupons of Al were pre-treated with different precursors and the painted with commercial enamel. Of the two possible approaches, the six-cut reticulated approach (25 squares) was followed. The test was performed using a commercial cutter and later refined using a standardized kit for the ASTM protocol. The test provides for a simple quantitative technique for assessing the adhesion properties of treated coupons. A standard light microscope was used to examine the samples. Typical samples are shown in Figure 2.

Five (5) replicates were made for the same precursor prepared in different molecular ratio proportions. Preliminary results compiled in Figure 3, indicate a strong correlation between the coatings and adhesion properties for commercial paints. Further analysis and comparison with different substrates is needed to draw more conclusive results.

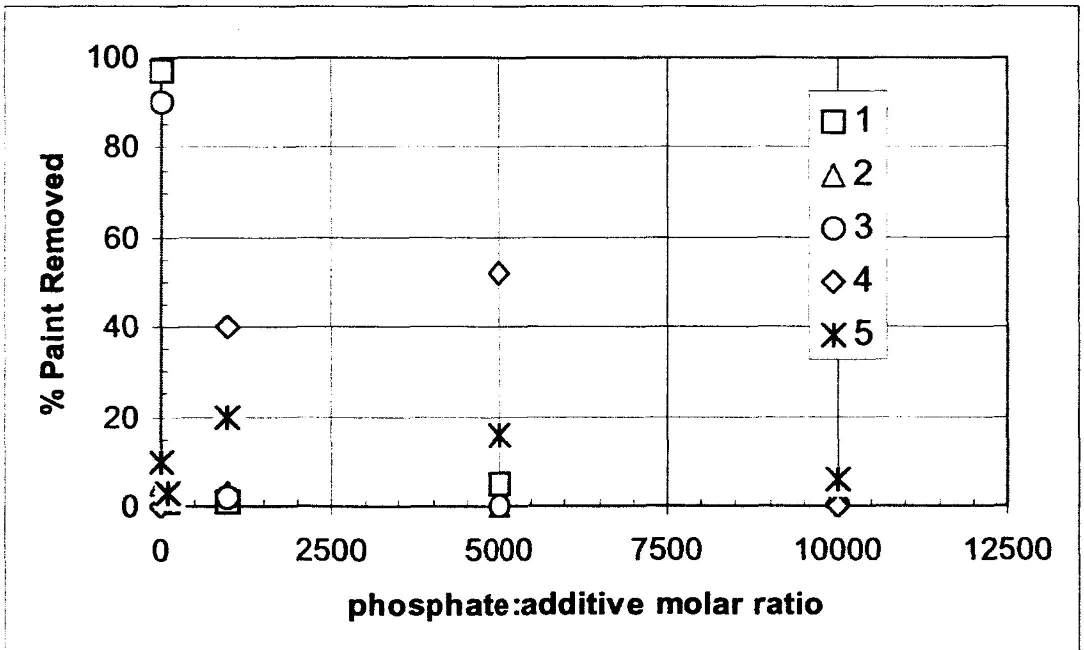

Figure 3: Tape test adhesion results

24-Hour Corrosion Testing

A 3.5 wt% solutions of NaCl-distilled water were used in the corrosion experiment. The pictures in Figure 4 resemble the following situations from left to right: untreated sample, sample with coating, untreated sample after 24-hour corrosion (one can see that the surface has started to form pits from the salt induced corrosion), and sample with coating after 24-hour test (where other than the blotches, no other surface modification can be seen).

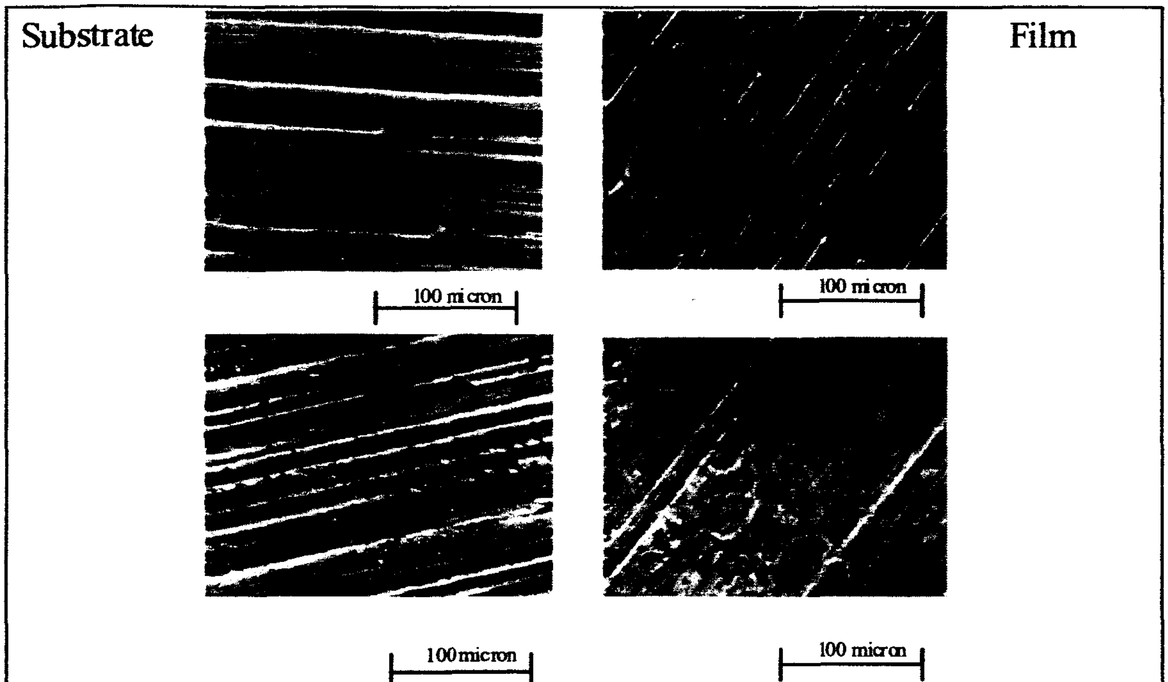

Figure 4: SEM images of Al 5052 samples subject to corrosion tests

Significance and Interpretation of Results

A CVD method was successfully developed to produce conversion coatings on aluminum alloys surfaces with reproducible results with a variety of precursors. A well defined protocol to prepare the precursor solutions formulated in a previous research was extended to other additives. It was demonstrated that solutions prepared following such a protocol could be used to systematically generate protective coatings onto aluminum surfaces. Experiments with a variety of formulations revealed that a refined deposition protocol yields reproducible conversion coatings of controlled composition. A preliminary correlation between solution formulations and successful precursors was derived.

Coatings were tested for adhesion properties enhancement for commercial paints. A standard testing method was followed and clear trends were identified. Only one precursors was tested systematically. Anticipated work on other precursors should allow a better characterization of the effect of intermetallics on the production of conversion/protective coatings on metals and ceramics.

The significance of this work was the practical demonstration that chemical vapor deposition (CVD) techniques can be used to systematically generate protective/conversion coating on non-ferrous surfaces. In order to become an effective approach to replace chromate-based pre-treatment processes, namely in the aerospace or automobile industry, the process parameters must be defined more precisely. Moreover, the feasibility of scale-up designs necessitates a more comprehensive characterization of the fluid flow, transport phenomena, and chemical kinetics interacting in the process. Kinetic characterization showed a significantly different effect of magnesium-based precursors when compared to iron-based precursors.

Future work will concentrate on refining the process through computer simulations and further experimental studies on the effect of other transition metals to induce deposition of conversion/protective films on aluminum and other metallic substrates.