[AMT04] Surface Composition and Morphology of Layered Double Hydroxide-based Composite Conversion Coating on Aluminum Alloy - an XRD and SEM Study

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Introduction

For particular functions, the natural surface oxide film of aluminum (Al) alloys is treated to form a functional conversion coating (CC). The functional CCs increase the adhesion of the subsequent organic layers such as paint and adhesive (Thompson, 1994). For example, in the widely employed chromate conversion coating (CCC), the "blade-like" surface morphology acts to interlocks the secondary coating, thus enhancing the adhesion (Leggat *et al.*, 2002a&b). However, the use of hexavalent chromium in the CCC systems is associated with toxicological problems that require significant expenditures in their handling and disposal (Friberg *et al.*, 1986).

Layered double hydroxides are inorganic materials made-up of alternating counter-charged nanolayers. The two-dimensional hydroxide lamellae are positively charged and form interlayer regions that are able to accommodate various anionic species such as CO_3^{2-}, NO_3^-, and Cl^-. Due to the weak electrostatic interaction, the anions can be substituted with an organic species via various routes (Cavani *et al.*, 1991; Rajamathi *et al.*, 2001). The resulting material of the substitution is called nanocomposite, made-up of inorganic host interleaved with organic guests at nanoscale regime (Figure 1). Layered double hydroxides are found to possess a microscopic surface morphology similar to that of the CCC. In addition, they are known as non-toxic materials.

In this study, an *in-situ* method was employed to develop a thin film of either a Zn-Al-nitrate layered double hydroxide (LDH) and/or a dye-interleaved-LDH nanocomposite (NC) on a pretreated, commercially pure aluminum alloy (AA1100) substrate. The idea of the process is to develop a new kind of composite CC on the substrate, primarily to enhance the surface properties related to the surface morphology and composition, particularly paint adherence, optical appearance and corrosion resistance.

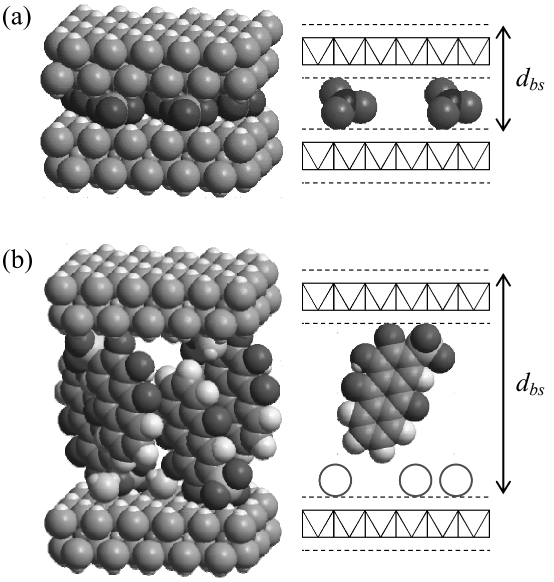

FIGURE 1. Computer-simulated models of LDH (a) and NC (b), showing expanded basal spacing (d_{bs}) upon the intercalation of dye molecules.

Materials and Methods

Synthesis of LDH and Nanocomposite

The LDH was synthesized using a self-assembly method. This is accomplished by titration of sodium hydroxide solution into a mother liquor under stirring, a mixed aqueous solution of zinc/aluminum nitrate salts (Zn/Al, R = 3.0), under nitrogen atmosphere. The final pH was controlled to 7.50 ± 0.02. The following process was the aging of the suspension of the as-precipitated LDH in an oil-bath shaker at 70 °C for 18 hours. The precipitate, white in color, was collected, thoroughly washed, completely dried, ground into fine powder and kept for further characterizations.

The NC was prepared using the same method, except an extra portion of an anionic dye, Alizarin Red S (ARS) was included into the mother liquor. As result, a reddish purple precipitate was obtained.

In-situ formation of LDH- and NC-CCs

For the formation of the CCs, pieces of solvent-degreased AA1100 alloy (1”×2”) were pretreated with caustic etching using 0.50 M NaOH solution for 15 minutes, desmutted using 10 % HNO_3, washed and dried. Shortly after the pretreatment, the alloy substrates were partially immersed into the coating bath (mother liquor) of either LDH or NC. This is followed by titration using NaOH solution to pH 7.50 ± 0.02 under condition identical for LDH and NC preparation. After a predetermined period, the substrates were removed from the suspension, washed, dried, and kept for further analysis. Parameters namely mother liquor concentration and contact time were studied and is presented in this paper.

Physicochemical characterizations

The as-synthesized reference materials (LDH and NC) and the respective CC was investigated primarily using powder X-ray diffractometry (PXRD) and scanning electron microscopy (SEM). X-ray diffractograms of the samples were recorded using a Shimadzu XRD-6000 X-ray diffractometer with CuK_α radiation at 2^o/minute continuous scan, 30kV accelerating voltage and 30mA current. Electron micrographs of the gold-coated specimens were recorded using a LEO 1445 VP scanning electron microscope at various magnifications, 20kV voltage and working distance of 15 – 18 mm.

Results and Discussion

Reference materials

The X-ray diffractograms of the powdered samples confirmed the formation of LDH and NC by showing their characteristic basal spacing of 9.0 Å and 20.1 Å, respectively (Figure 2). The expanded basal spacing of NC was due to the intercalation of ARS into the interlayer of LDH host. The degree of expansion is dependent on the size, amount and orientation of ARS in the interlayer. The orientation of the ARS anions has been interpreted as a “vertical-orientation” based on the molecular modeling study. Figure 1 also showed that the measured basal spacing of NC is consistent with the sum of the thickness of LDH lamella (4.8 Å), ARS anion (12.4 Å) and a crystalline water layer (2.8 Å).

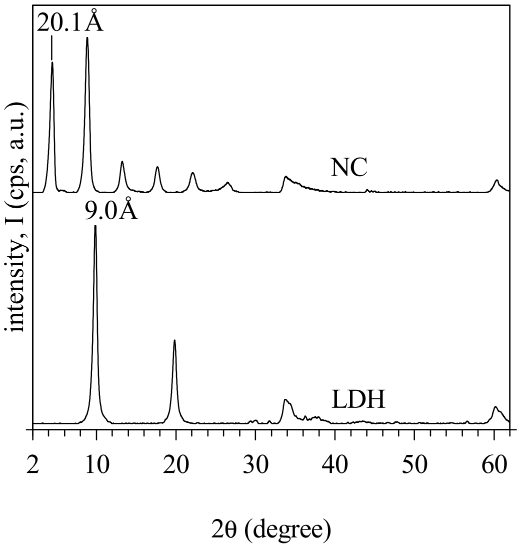

FIGURE 2 PXRD patterns of LDH and NC, showing the respective basal (003) diffractions.

The SEM micrographs (Figure 3) of the materials show distinctive morphologies between the LDH and NC. Flaky morphology comprises of scale-shaped microcrystallites was observed for LDH. However, a unique “fibrous” morphology comprises of undefined grains was observed for NC. The abrupt change in microscopic morphology was interpreted as a result of the intercalation of ARS anions into the lattice of LDH, which has altered the nucleation, crystallization and agglomeration process.

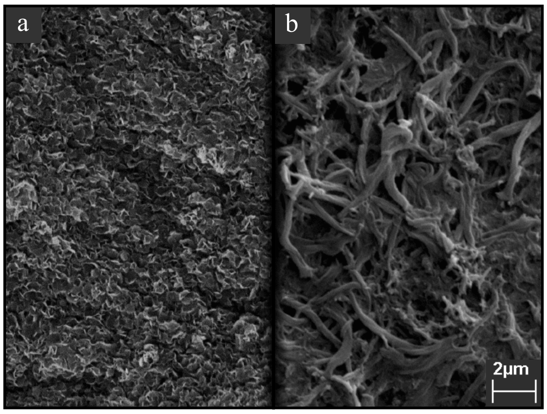

FIGURE 3 SEM micrographs of LDH (a) and NC (b), showing distinctive microscopic morphology as a result of ARS-intercalation in the latter.

AA1100 Substrate

The degreased, caustic-etched and then desmutted AA1100 substrates show [111] and [200] diffractions at around 38.47° and 44.70°, respectively, which matched the JCPDS data card no. 04-0787. The pretreatment did not vary the diffraction degree very much. However, SEM micrographs (Figure 4) reveal that the surface morphology and topography of the substrate changed in accordance to the pretreatment steps.

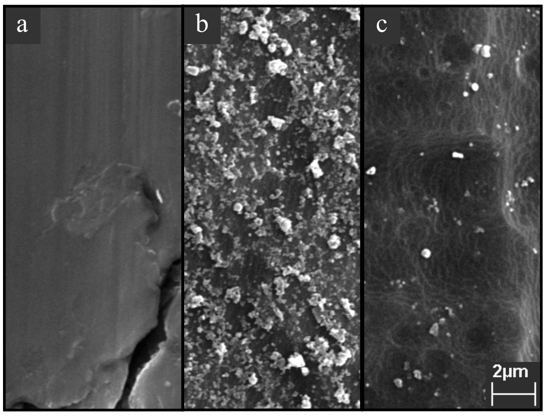

FIGURE 4 SEM micrographs of AA1100 surface after solvent-degreasing (a), followed by caustic-etching (b), and finally acidic-desmutting (c).

The solvent-degreased substrate shows smooth surface oxide film with some natural cracks. Caustic-etching removes the oxide film and some base aluminum, leaving a pitted surface covered with the alloying elements. Most of the alloying elements are removed after acidic-desmutting, leaving a relatively clean and bared aluminum base for the formation of the composite CCs.

LDH and NC conversion coating

The formation of the LDH-CC was shown in the PXRD study, where the first diffraction peaks of the substrate surface were identical to the basal (003) diffraction peak of powdered LDH (Figure 5). An increase in contact time from 15 to 90 minutes, as well as increasing the bath concentration, has resulted in higher diffraction peak intensities. This observation suggested the formation of either better-crystallized or thicker coating.

However, the formation of NC-CC cannot be detected using XRD technique due the low crystallinity of NC and the instrument detection limit.

Down to the microscopic scale, SEM micrographs revealed a highly roughened surface morphology of the coated substrates that matched those of the reference LDH and NC (Figure 6). The formation of the composite CC was therefore confirmed.

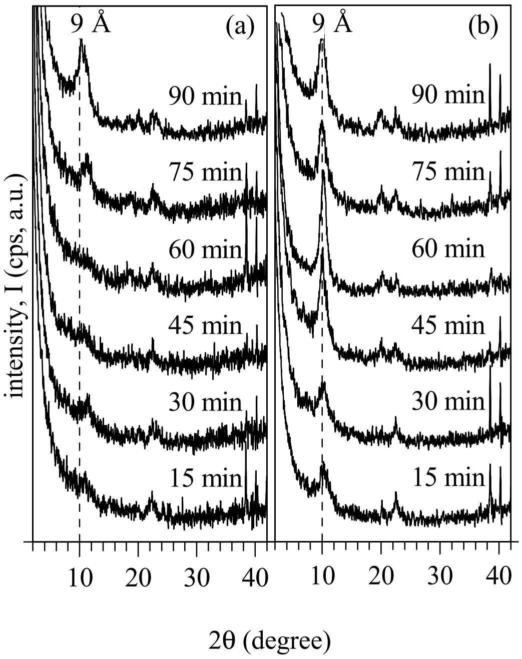

FIGURE 5 XRD patterns of LDH-CC prepared from coating bath concentration of 0.025M (a) and 0.050M (b). Increase in contact time resulted in higher diffraction peak intensity.

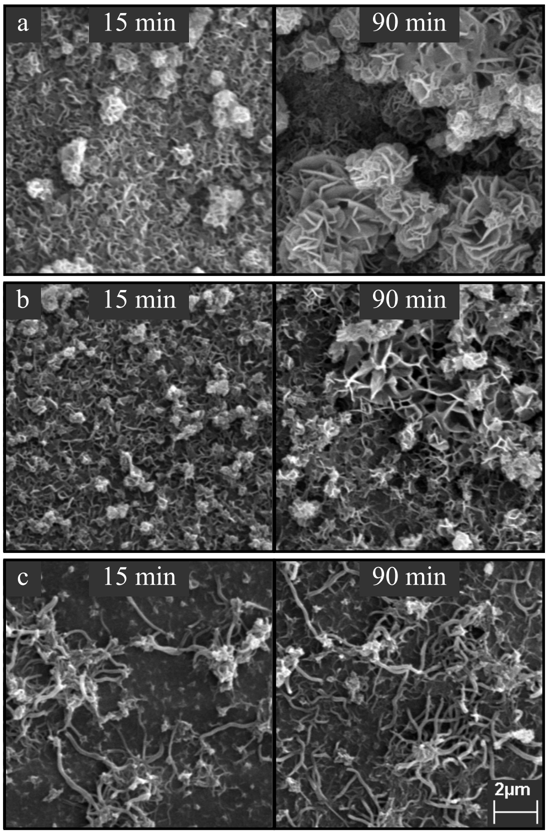

FIGURE 6 SEM micrographs of LDH-CC prepared from 0.025M bath (a), 0.050M bath (b), and NC-CC prepared from 0.025M bath (c).

As the contact time was increased, larger LDH microcrystallites were observed on the coated substrates for the studied bath concentrations; 0.025M and 0.050M solutions. This was attributable to the extension of crystal growth permitted as contact time increased. Only one concentration (0.025M) was studied in the formation of NC-CC. Similar to the LDH-CC, the increase of the contact time has resulted in a higher coverage of the “fibrous” NC grains over the substrate.

For LDH-CC, the increase in the contact time has also resulted in higher agglomeration of the microcrystallites. However, the LDH-CC prepared from the 0.050M bath showed less agglomeration, thus resulted in smoother surface topography.

The results of this study showed that the new type of non-toxic composite conversion coating for surface pretreated Al-alloys can be prepared by a simple self-assembly method. The thickness and morphology of the coating can also be tailor-made by varying the preparation parameters, namely contact time and bath concentration. As a result of the conversion process, highly roughened microscopic surface morphology of the substrate was obtained, which is expected to affect the physicochemical behaviors of the subsequent organic coating such as adherence and corrosion resistance.

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