THE STUDY OF SURFACE PHASES ON ALUMINIDE COATINGS USING X-RAY DIFFRACTION

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1. Background

Aluminide coatings are widely used to protect materials of construction subject to harsh operating conditions such as high temperatures and corrosive environments. Halide activated pack cementation (HAPC) is an economical way to produce aluminide coatings that enable materials to withstand a more corrosive environment [1]. Alumnide coating typically consisted of intermetallic compound. Intermetallic, such as AlFe, are good candidate to withstand catalytic coking, carburization, sulfidation and wear which has applications for piping in chemical industries [1] Studying the surface phase of the coating will give the insight on coating characteristics, in which the desirable phases can be selected by changing process parameters. X-ray diffraction (XRD) is a powerful tool that can be effectively used to investigate intermetallic compounds formed at the surface of the an aluminide coating.

2. Objective

To investigate the effect of activator and temperature on transformation of surface phases of the aluminide coating.

3. Hypothesis

The transformation of surface phases depends on coating temperature and the thermodynamic stability of activators.

4. Materials & Methods

3.1 Preparation of the pack

UNS S30400 austenitic stainless steel samples were metallographically prepared to a 600 grit finish. Mass and dimensions of the sample were recorded. The samples were then degreased and cleaned by ultra-sonication in methanol, followed by cleaning with soap and a demonized water rinse. A pack mixture of aluminum, aluminum oxide, and an activator (NH_4Cl, $AlCl_3$, NaCl, NaF, AlF_3, Na_3AlF_6) was prepared. The mixture was thoroughly crushed, then blended in a roller mill. The blended pack and the sample were then placed into an alumina crucible and sealed using ceramic cement. After a curing process, the pack was placed in a furnace and heated to temperatures of 650-850 °C for 9 hours. After the furnace cooled down, the pack was extracted from the furnace and opened to remove the sample. The sample was then thoroughly cleaned, dimensioned, and analyzed using X-ray diffractometry.

3.2 Characterization of coatings

The surface phases were identified by X-ray diffraction using a Cu Kα (λ = 1.540560 Å) radiation source, 40 kV tube voltage and the beam current of 44 mA. Data were collected by step scanning from 5° - 85 ° with step size of 0.02° (2θ). The surface phases and its quantity were analyzed using Whole Pattern Fitting, with a linear background function.

5. Result

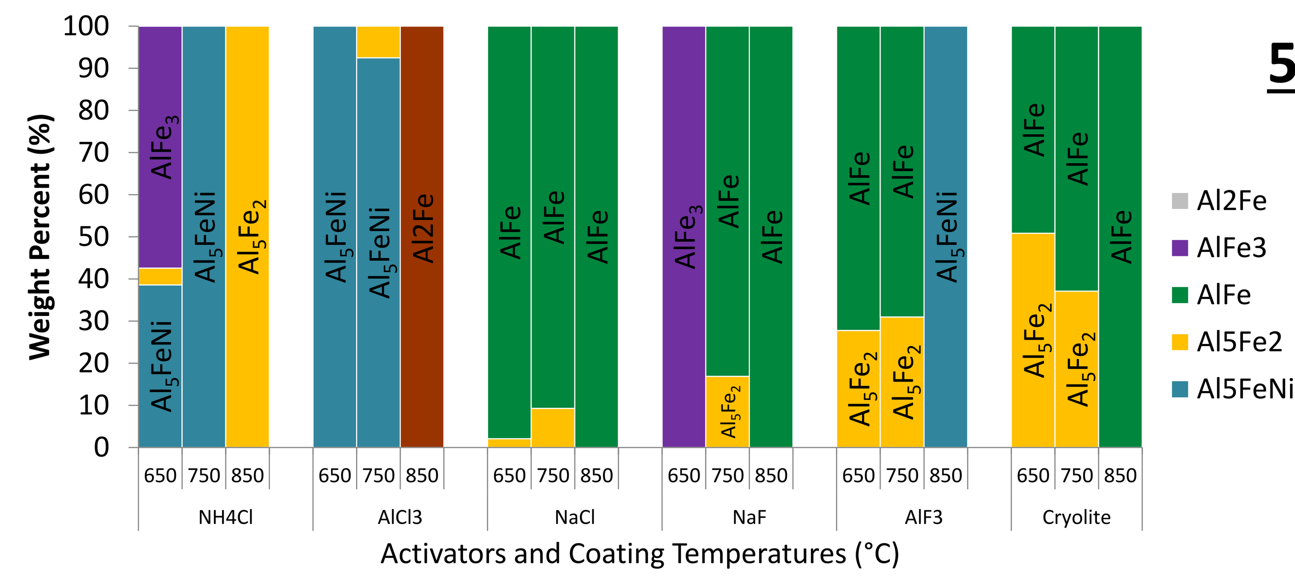

Figure 1 : The amount of surface phases quantified using whole pattern fitting method

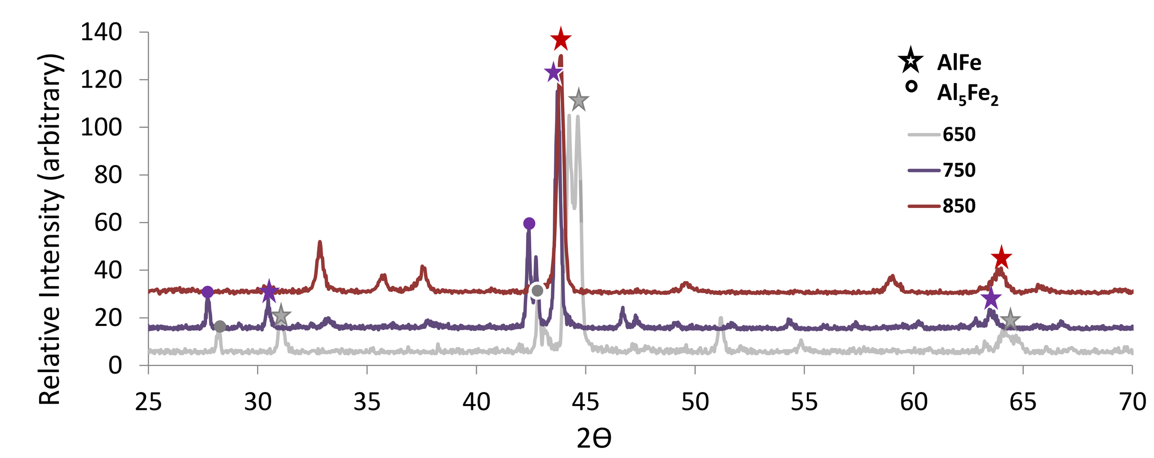

Figure 5: XRD patterns of UNS S30400 coupon coated with Na_3AlF_6 activators at three different temperatures

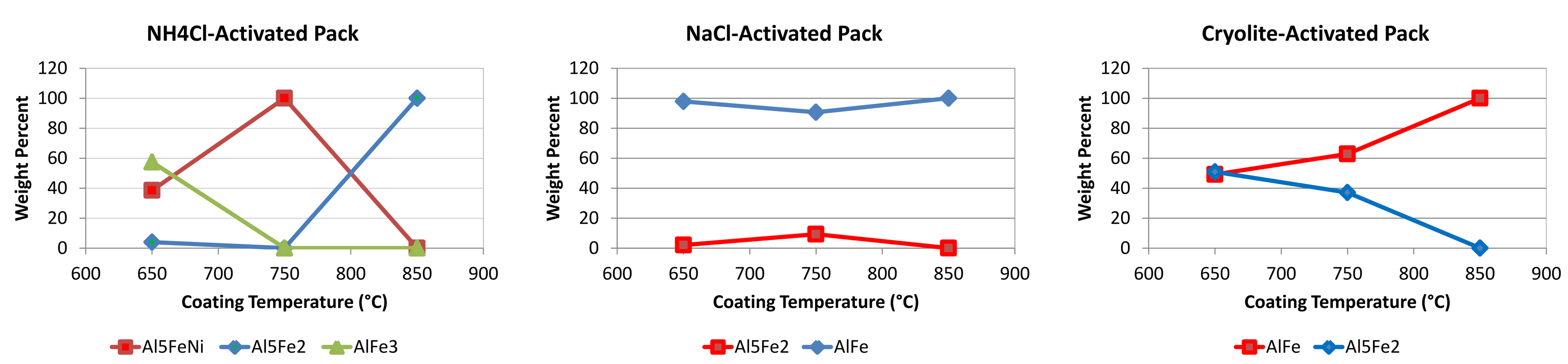

Figure 2 : The effect of coating temperature on surface phases coated in packs using different activator (a) NH_4Cl (b) NaCl (c) Na_3AlF_6 (cryolite)

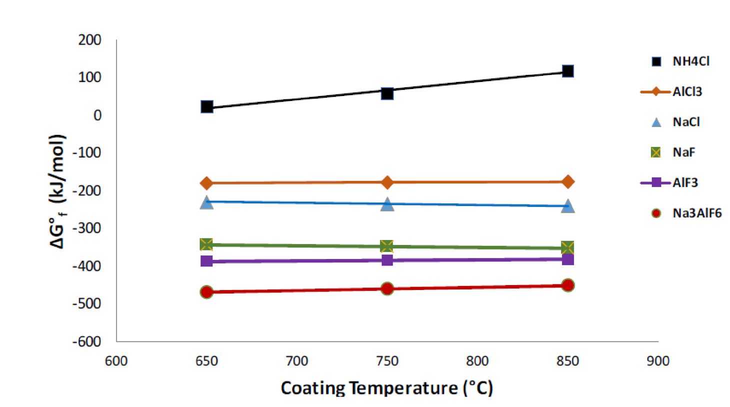

Figure 4 : The standard Gibbs free energy calculated per mole of halide [3]

6. Discussion

The results indicate that process temperatures and the thermodynamic stability of the activator affect both the type and composition of the surface phases. In general, the aluminide coatings exhibit multiple phases at the lower coating temperature (650°C) and transform into a single phase at the higher coating temperature (850°C). Figure 1 maps out the different phases formed as a function of coating temperatures and activators. Surface phases produced using NH_4Cl, undergo the most number of transformations, in regard to the dominant phase, the temperature range studied (Figure 2). At 650°C, the NH4Cl-activated pack produces three phases with $AlFe_3$ as the most prominent phase (57.4 wt%) co-existing with Al_5FeNi (38.6 wt%) and Al_5Fe_2 (4.0 wt%). When the coating temperature was increased to 750°C, these multiple phases evolved into an aluminum rich phase (Al_5FeNi) that transformed into Al_5Fe_2 at 850°C. Similar phase transformation behavior in NaCl-and Na3AlF6-activated packs were observed. At 650°C, Al_5Fe_2 (97.9 wt%) and AlFe (2.1 wt%) were formed. When the coating temperature increased to 750°C and 850°C, AlFe remained as the most abundant phase. Increased amount of the AlFe intermetallic was observed with increases in coating temperature. This is supported by the observation of higher peak intensities for the AlFe phase (Figure 3). The nature of the phase transformation in NH4Cl-, NaCl-, and Na3AlF6- activated packs could be further understood by examining the thermodynamic stability of these salts (Figure4). NH4Cl is the least stable activator when compared to NaCl and Na_3AlF_6. Therefore, the stability of activator plays an important role in the nature and amount of the surface phases. The most stable activator maintains a stable pack atmosphere thereby resulting in more gradual changes at the surface. The unstable activator, on the other hand, is likely to create changes in the pack atmosphere, thereby resulting in more changes at the surface.

7. Summary and Conclusions

The surface phases of aluminized UNS S30400 were successfully quantified using XRD. The whole pattern fitting method revealed that Al_5Fe_2 is the most common phase for all process parameters utilized in this study. Al_5Fe_2 and AlFe were observed to co-exist when NaCl, NaF and Na_3AlF_6 activators were used. The thermodynamic stability of the activators was found to have an impact on the prominent phase of the coating, e.g. the prominent phase formed using the least stable activator (NH_4Cl), is $AlFe_3$ at 650°C, Al_5FeNi at 750°C and Al_5Fe_2 at 850°C. However, for the most stable activator (Na_3AlF_6), the prominent phase is AlFe for all coating temperature.

8. Future Work

XRD analysis will be used to further investigate the following areas:

a) Effect of surface roughness on XRD pattern generation
b) Crystallite size determination
c) Residual stress determination

9. References

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2) N.S. Stoloff, C.T. Liu, S.C. Deevi. Emerging applications of intermetallics. Intermetallics, 8 (2000): 1313-1320
3) Pankratz, L. B. Thermodynamic Properties of Halides. Washington: U.S. Dept. of the Interior, Bureau of Mines, 1984. Print

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