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## IMPROVED THERMAL STABILITY OF Al-Si ALLOY COATED STEEL SHEET WITH Cr THIN FILM DEPOSITION

We investigated the effect of Cr thin film deposition on the thermal stability and corrosion resistance of hot-dip aluminized steel. A high-quality Cr thin film was deposited on the surface of the Al-9 wt. % Si-coated steel sheets by physical vapor deposition. When the Al-Si coated steel sheets were exposed to a high temperature of 500°C, Fe from the steel substrate diffused into the Al-Si coating layer resulting in discoloration. However, the highly heat-resistant Cr thin film deposited on the Al-Si coating prevented diffusion and surface exposure of Fe, improving the heat and corrosion resistances of the Al-Si alloy coated steel sheet.

*Keywords:* Aluminized steel; Physical vapor deposition; Cr thin film; Corrosion resistance; Thermal stability

### 1. Introduction

Hot-dip Al-Si alloy coated steel sheet has excellent corrosion and heat resistances owing to the passivation effect of the Al<sub>2</sub>O<sub>3</sub> layer formed on the surface in corrosive environments [1-5]. It can be used without discoloration at temperatures higher (approximately 100-150°C) than that of conventional galvanized steel sheet [6-8]. Hence, Al-Si alloy coated steel sheets are widely used in the manufacture of industrial products exposed to high-temperature environments, such as automotive exhaust components and heating systems [9-11]. To meet the increasing demand for steel sheets in applications involving high temperatures and corrosive environments, current research is focused on diffusion barrier coatings and development of novel coating systems [9,12,13]. When a steel substrate coated with a heterogeneous metal, such as Al and Zn, is exposed to high temperatures, the Fe from the substrate diffuses into the coating layer and is exposed to the surface. The diffused Fe forms Fe-based oxides on the surface in a corrosive environment, which accelerates discoloration and corrosion [9,14]. In this study, we propose the use of a highly heat-resistant Cr thin film as a diffusion barrier to prevent surface exposure of Fe (diffused from the steel substrate) and improve the thermal stability and corrosion resistance of hot-dip Al-9 wt.% Si-coated steel sheets.

Heat resistance test and salt spray test (SST) were performed to compare and evaluate the properties of the Al-Si alloy coated steel sheets before and after the deposition of Cr thin film.

### 2. Experimental

Hot-dip Al-9 wt.% Si coated steel sheets (POSCO STEEL-LEON Inc.) were used as the substrates. A thin Cr film was deposited on the Al-Si alloy coated steel sheet at room temperature by thermal evaporation from a 99.95 % pure Cr pellet source at 0.35 kW for 1 h. Prior to the deposition, the chamber was evacuated to a base pressure of  $1 \times 10^{-5}$  Torr. The samples (150 mm × 30 mm) were ultrasonically degreased by immersing in acetone, ethanol, and deionized water for 10 min each, followed by air blowing. Two types of samples were prepared. The first sample was a reference sample without the Cr thin film (referred as 'AlSi'). The second sample was coated with a Cr thin film (referred as 'AlSi-Cr'). The thickness of the Cr layer was approximately 300 nm. The heat resistance test was conducted using an electric furnace at 500°C for 24 h in air ambient. The microstructural features before and after the heat resistance test were observed using a field-emission scanning electron microscope (FE-SEM; SUPRA40VP, Carl Zeiss).

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The changes in the surface roughness of the samples after the heat resistance test were studied using a three-dimensional (3D) optical surface profiler (SURFiEW 1000C, GL-Tech). Energy dispersive X-ray spectroscopy (EDS) was used to analyze the elemental compositions of the coatings. A SST was conducted according to international standard ASTM B117 to evaluate the corrosion resistance. Before the SST, the cut edges of the sample were insulated with tape; the exposed area of the sample was 5 cm × 3 cm. The temperature inside the chamber was maintained at 35 °C, and an aqueous solution of 5 wt.% NaCl was used for salt spraying.

### 3. Results and Discussion

Fig. 1 shows the cross-sectional FE-SEM images of AlSi and AlSi-Cr. As shown in Fig. 1(a), the Al-9 wt. % Si coating layer is composed of the Al-Si eutectic phase with randomly distributed  $\tau_5$ -Fe<sub>2</sub>Al<sub>7</sub>Si intermetallic compounds. At the interface between the coating and substrate, intermetallic layers such as  $\eta$ -Fe<sub>2</sub>Al<sub>5</sub>,  $\tau_1$ -Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>, and  $\tau_5$ -Fe<sub>2</sub>Al<sub>7</sub>Si were formed by Fe elution during the hot dipping process [1,15-17]. As shown in Fig. 1(b), Cr deposition did not change the microstructure of the Al-Si coating layer. After the heat resistance test (Fig. 1(c)), the interdiffusion between the substrate and the coating layer resulted in the formation of a thick Al-Si-Fe intermetallic

layer, with the  $\eta$ -Fe<sub>2</sub>Al<sub>5</sub> phase accumulated near the substrate,  $\tau_1$ -Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub> phase widely distributed in the middle, and  $\tau_5$ -Fe<sub>2</sub>Al<sub>7</sub>Si alloy phase confined near the coating surface [17,18]. It is noteworthy that many pores and cracks were formed near the surface of AlSi after the high-temperature heat treatment. The formation of high-density Al-Si-Fe alloy phases at a high temperature causes shrinkage of the coating layer, resulting in the formation of cracks and voids inside the coating layer [18]. However, the Cr thin film was undamaged and efficiently suppresses the formation of cracks in the coating layer, as shown in Fig. 1(d).

The surface microstructure and topography before and after the heat resistance test were studied using FE-SEM and 3D surface profiler, respectively, and the results are shown in Fig. 2. The formation of Al-Si-Fe alloy phases and surface shrinkage during the heat treatment significantly affected the surface morphology of the coatings. The root mean square roughness ( $R_{rms}$ ) values of the AlSi sample before and after the heat resistance test are 0.96 and 3.14  $\mu\text{m}$ , respectively. In contrast, the high-temperature heat treatment did not affect the surface topography of the Cr thin film significantly. The  $R_{rms}$  values of the AlSi-Cr sample before and after the heat resistance test are 0.94  $\mu\text{m}$  and 1.01  $\mu\text{m}$ , respectively.

Fig. 3 shows the EDS line scan results of the cross-sections of the coatings before and after heat treatment. The Fe content in the AlSi and AlSi-Cr coating layers before heat treatment

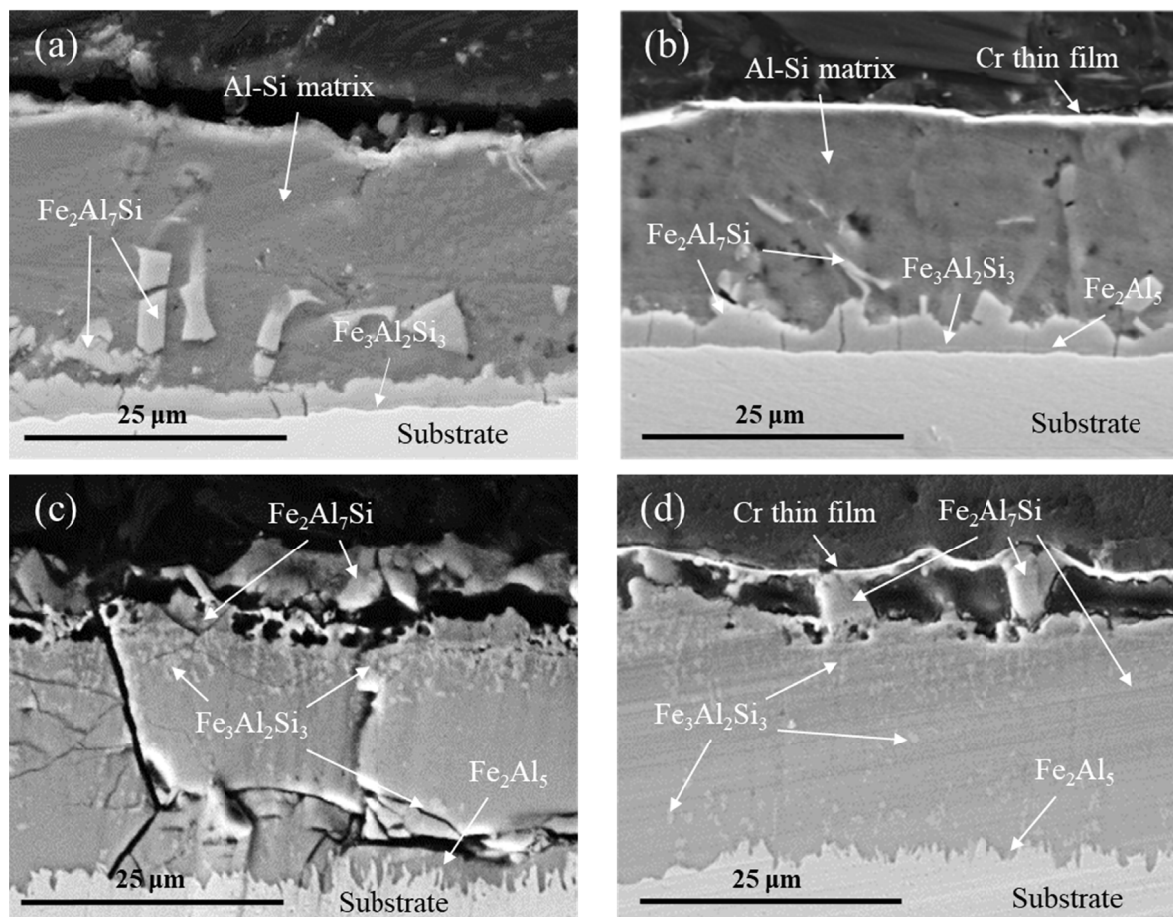


Fig. 1. Cross-sectional FE-SEM images of AlSi and AlSi-Cr (a, b) before and (c, d) after the heat resistance test, respectively

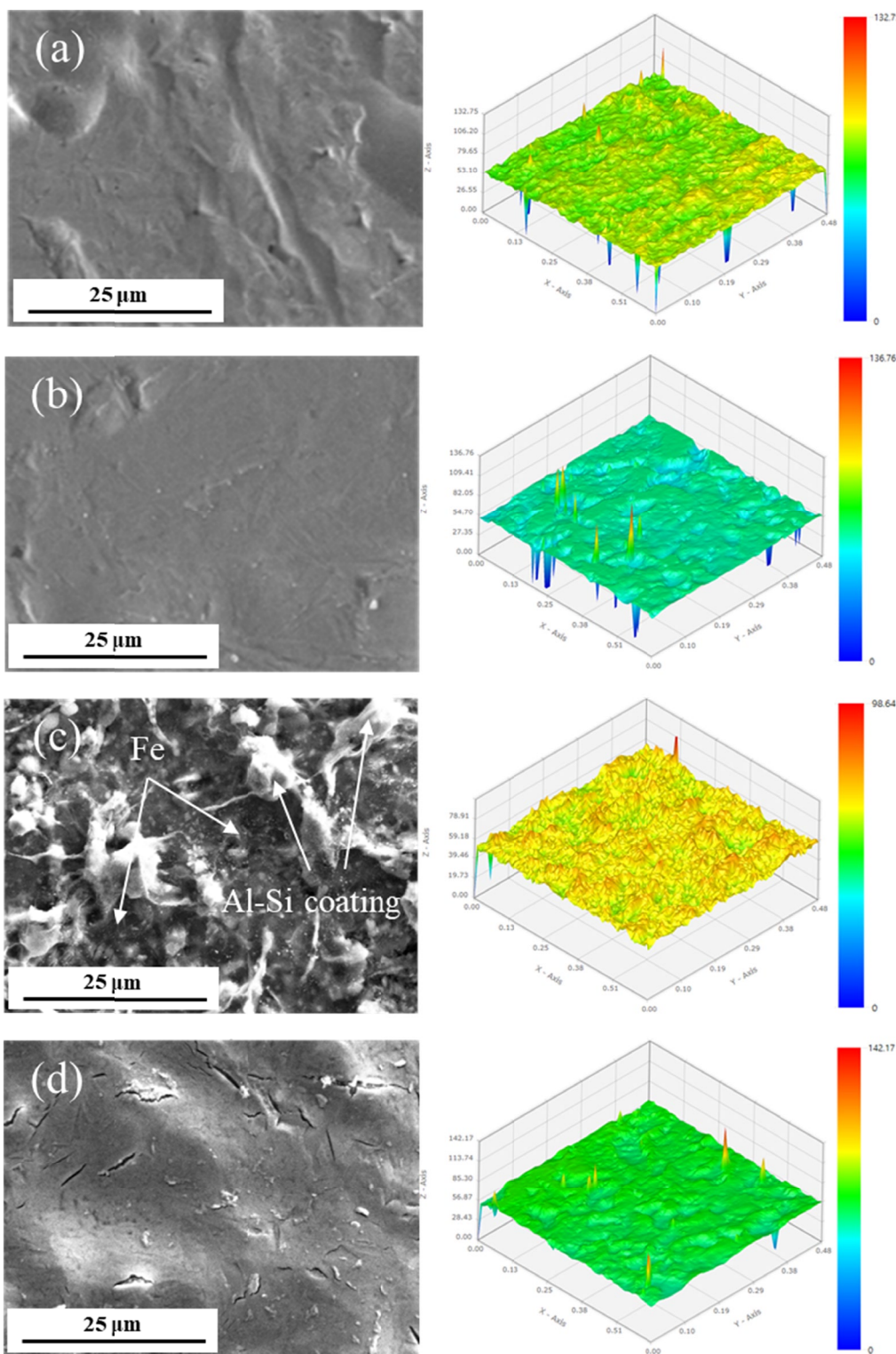


Fig. 2. Top-view FE-SEM images and 3D surface profile images of AlSi and AlSi-Cr (a, b) before and (c, d) after the heat resistance test, respectively

originates from the intermetallic layer between the coating and substrate and is intermittently detected in the coating layer because of the presence of  $\tau_5\text{-Fe}_2\text{Al}_7\text{Si}$  phase. However, the Fe in the substrate diffused out into the coating layer after the heat resistance test. It is evident from Fig. 3(e) that Fe in AlSi reached the surface of the Al-Si coating. In contrast, Cr remained at the surface during high-temperature heat treatment and effectively prevented Fe from diffusing to the surface.

TABLE 1

Surface elemental compositions of AlSi and AlSi-Cr before and after the heat resistance test

Sample	Composition (wt.%) before heat resistance test				Composition (wt.%) after heat resistance test			
	Al	Si	Cr	Fe	Al	Si	Cr	Fe
AlSi	84.30	14.73	—	0.97	62.18	11.34	—	26.48
AlSi-Cr	34.35	8.35	56.56	0.74	35.21	4.29	58.04	2.46

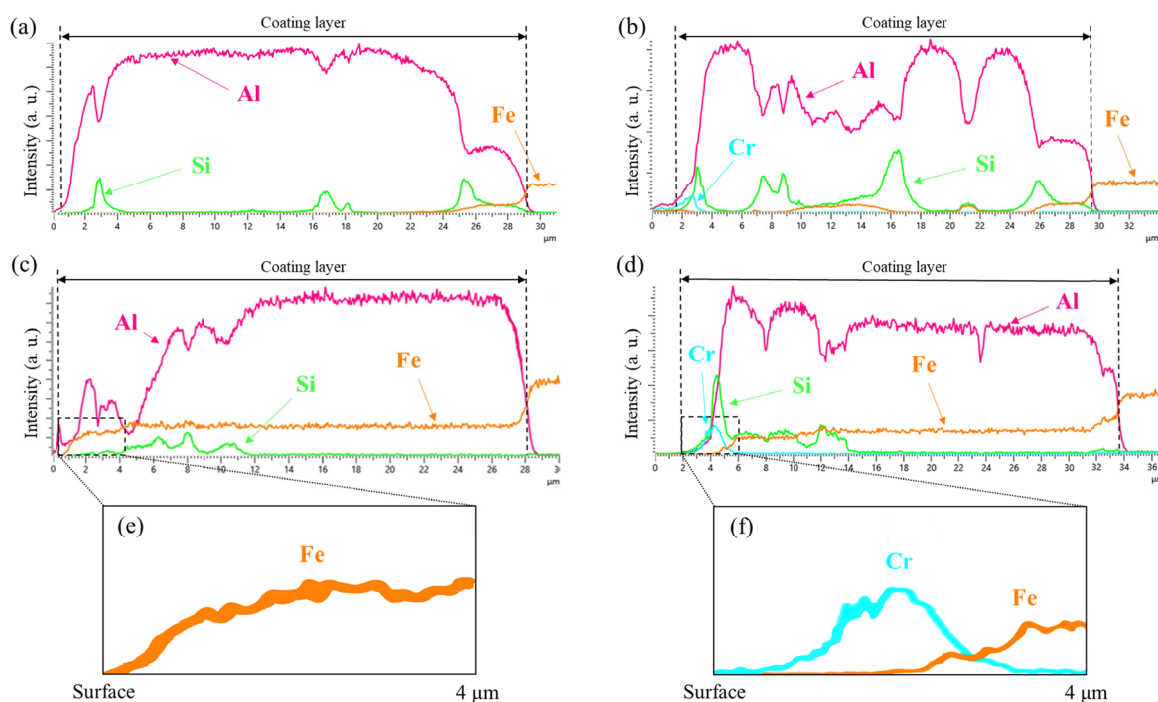


Fig. 3. EDS line scan profiles of cross-sections of AlSi and AlSi-Cr (a, b) before and (c, d) after the heat resistance test, respectively. (e) and (f) Magnified profiles of the squared regions in (c) and (d), respectively

To confirm the diffusion barrier property of the Cr thin film, the surface elemental compositions before and after the heat resistance test were analyzed by EDS, and the results are shown in Table 1. Before the heat resistance test, the surface Fe contents of the AlSi and AlSi-Cr samples were 0.97 and 0.74 wt.%, respectively. After the heat resistance test, 26.48 wt.% Fe was detected in AlSi, indicating the surface diffusion of Fe after heat treatment, which is consistent with the FE-SEM and EDS line scan results. However, only 2.46 wt.% Fe was detected on the surface of AlSi-Cr after the heat resistance test, confirming the effective prevention of Fe diffusion by the Cr thin film.

Fig. 4 shows the SST results of the samples subjected to the heat resistance test. In AlSi, Fe diffused to the surface during heat treatment, and red rust caused by the formation of Fe-based corrosion products was observed within 24 h, indicating its inferior corrosion resistance. Contrarily, red rust was not observed in AlSi-Cr even after 120 h of SST, indicating its high thermal stability and corrosion resistance.

#### 4. Conclusions

We investigated the effect of Cr thin film deposition on the thermal stability of Al-9 wt.% Si coated steel sheet. During the heat resistance test at 500°C, interdiffusion between the substrate and the coating resulted in the formation of a thick Al-Si-Fe intermetallic layer. The diffusion of Fe from the substrate to the surface deteriorated the heat and corrosion resistances of the Al-Si alloy coated steel sheet. The deposition of a highly heat-resistant Cr thin film effectively suppressed the diffusion of Fe and improved the thermal stability of the Al-Si alloy coating.

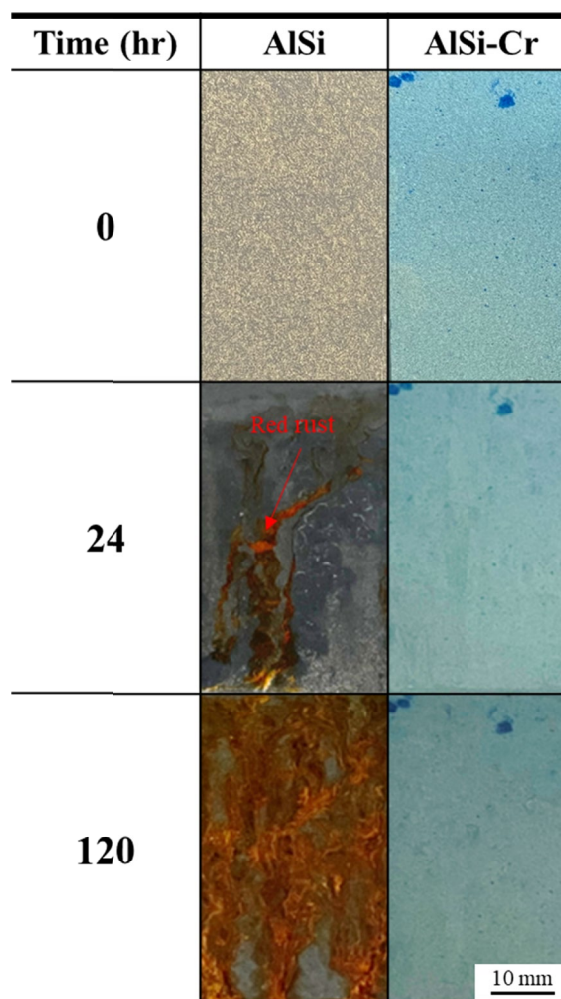


Fig. 4. Results of the salt spray test of AlSi and AlSi-Cr after the heat resistance test

In addition, AlSi-Cr also showed improved corrosion resistance than AlSi. These results indicate that the deposition of Cr thin film on the alloy coating surface can improve the corrosion resistance and thermal stability of the hot-dip Al-Si coated steel sheet for applications in high-temperature and highly corrosive environments.

#### Acknowledgments

This work was supported by the [National Research Foundation of Korea (NRF)] grant funded by the Korea Government (Ministry of Science and ICT) [No. 2022R1A2C1008972]. This work was also supported by the Technology Innovation Program (20012941) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). This work was also supported in part by the Technology Development Program (00221849) funded by the Ministry of SMEs and Startups (MSS, Korea). This work was also supported in part by “Research Base Construction Fund Support Program” funded by Jeonbuk National University in 2023.

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