

Hydrophilic Coating with Water glass and Sodium Poly-acrylate on the Aluminum Sheet with Chromate-phosphate Conversion Coating

Yosuke Ota¹ and Takahiro Shimizu¹

¹Aluminum Sheets & Coil Research Department, Moka Plant, Aluminum & Copper Company, KOBE STEEL, LTD., 15 kinugaoka, Moka, Tochigi 321-4367, Japan

Hydrophilic coating for aluminum fin-stock with water glass (i.e. sodium silicate) and sodium poly-acrylate were applied onto the aluminum sheet with pretreatment of chromate-phosphate conversion coating. The coated aluminum sheet was then baked and repeatedly dipped into distilled water (denoted as wet-dry cycle) to evaluate the elution, hydrophilicity and surface morphology of silica film. Cr weight of chromate-phosphate conversion coating for pretreatment was varied and surface free energy and FT-IR spectra of each Cr weight were studied to correlate the pretreatment with resultant surface property of silica film. It was clarified that when Cr weight increased, silica film showed better hydrophilicity after wet-dry cycles and surface morphology of silica film looked more continuous with pores rather than fragmented domain, which was analogously compared with co-continuous structure formed by spinodal decomposition in macroporous silica monolith synthesis. Surface of chromate-phosphate conversion coating with larger Cr weight showed higher surface free energy of polar component and indicated the existence of more abundant hydroxyl group according to FT-IR analysis. Difference of surface free energy of polar component on the conversion coating was considered to have affected the phase separation of water-glass and sodium poly-acrylate during solvent evaporating process of hydrophilic coating, which determined the resultant hydrophilicity of silica film.

Keywords: *hydrophilicity, chromate-phosphate conversion coating, spinodal decomposition, surface free energy, silica film.*

1. Introduction

Fin-and-tube heat exchangers with hydrophilic coating are widely used for air-conditioner. Typical aluminum fin-stock is made of commercial-purity aluminum (1200) coiled sheet with about 0.1 mm gauge which is usually pre-coated in view of corrosion resistance, press formability [1] and hydrophilicity. When a heat exchanger works as an evaporator, condensed water is generated on chilled fin in usual humidity and this condensate does not bridge the inter-fin gap about 1.2 to 2.0 mm if the coating on aluminum sheet has enough hydrophilicity, which contributes to smooth air-flow through the heat exchanger and the better performance of air-conditioner [2]. Thus hydrophilicity of the coated surface is one of the most important properties for the aluminum fin-stock.

Various types of hydrophilic coating for aluminum fin-stock have been proposed; typical one is the organic resin type coating for indoor application which does not deteriorate its hydrophilicity at the atmosphere with volatile organic compounds that comes from residential materials, and the other is silicate type coating mainly for outdoor application which has basically superior hydrophilicity because of its macroporous morphology at the atmosphere without volatile organic compounds [2]. Among them, silicate type coating of water glass (i.e. sodium silicate) with poly-acrylic acid onto the aluminum sheet that has pretreatment of chromate-phosphate conversion coating, with water-soluble lubricant coating layer for press formability (Fig.1), has been widely in commercial use. The chromate-phosphate conversion coating is made up from $\text{Cr}(\text{OH})_3$, CrPO_4 , $\text{Al}(\text{OH})_3$, and AlPO_4 [2]. It is used as a common pretreatment for aluminum can end stock for beer or beverage etc.[3], because it provides superior corrosion resistance and film adhesiveness. And it contains only trivalent Cr and is free from hexavalent one. It was previously reported that surface morphology and resultant

hydrophilicity of silica film were strongly dependent on Cr weight [3], but the variation of the surface property of the conversion coating with Cr weight was not investigated and the mechanism associated with silica film formation was not discussed.

In this work, sodium poly-acrylate (MW=200,000) was used for silicate type coating instead of poly-acrylic acid (MW=20,000) which was used previously [4] in order to avoid spontaneous gelation of water glass by acidity of poly-acrylic acid and eventually to obtain uniform coated film. Pretreatment of chromate-phosphate conversion coating with varied Cr weight was performed prior to the above hydrophilic coating. Then the influence of Cr weight on the property of silica film was investigated and mechanism of the silica film formation is discussed in detail.

2. Experimental

As for pretreatment, JIS A1200P aluminum sheet was dipped into NaOH based solution to remove the mill oil, dipped into deionized water for rinse, dipped into a bath of "Alsurf 401/45" at room temperature made by Nippon Paint CO., LTD., which formed a chromate-phosphate conversion coating, and dipped into deionized water again for rinse. Cr weight of the conversion coating was adjusted by controlling the dipping duration into the bath of "Alsurf 401/45". Then the aqueous solution of water glass with sodium poly-acrylate was coated with bar-coater so that SiO₂ weight would be 250 mg/m² after drying process in the furnace at 200 °C with air-blow for 9 seconds. For water glass, No.3 in Japanese Industrial Standards (JIS), containing 29wt% SiO₂ and 10wt% Na₂O, made by Fuji chemical CO., LTD. was used. For sodium poly-acrylate, average molecular weight (MW) of 200,000, made by Toagosei CO., LTD. was used. Four types of sample sheets, including the sample without conversion coating process, were prepared as listed in Table 1.

Elution of silica and sodium in hydrophilic coating after wet-dry cycles (i.e., dipped into deionized water for 24hrs and dried for 30 minutes at room temperature; up to 5 cycles) was examined by X-ray fluorescence analysis. Surface morphology was studied by SEM, which were correlated with hydrophilicity by contact angle measurement.

Surface of chromate-phosphate conversion coating with varied Cr weight (without hydrophilic coating) was characterized by surface free energy, which was figured out by measuring contact angles of some polar (i.e. water, glycerol, formamide and methyleneiodide) and non-polar (i.e. n-hexadecane and nonane) liquids, and was also characterized by FT-IR analysis.

Lubricant resin film layer (water-soluble)
Hydrophilic silica film layer (macroporous morphology)
Chromate-phosphate conversion coating
Aluminum substrate

Fig.1 An example of cross-section image of typical pre-coated aluminum fin-stock with silicate type coating, which has layered composition.

Table 1 Sample preparation

Code.	Cr weight of the conversion coating (mg/m ²)	Silica weight of the hydrophilic coating (mg/m ²)
(a)	0	250 *Weight ratio: silica in water glass / sodium poly-acrylate = 10 / 5
(b)	10	
(c)	25	
(d)	70	

*Lubricant resin layer, which is soluble in water, was not applied for the above samples, as it does not affect the hydrophilicity after wet-dry cycles.

3. Results and discussion

Residual sodium and remaining silica in hydrophilic coating after wet-dry cycles is graphically shown in Figure 2 and Figure 3. Sodium is finally rinsed off by wet dry cycles but it is also clear that

sodium in the silica film on Cr-rich conversion coating tends to remain after wet-dry cycles. Silica with conversion coating is not eluted by wet-dry cycles regardless of the amount of Cr weight, while silica without conversion coating is partially eluted by wet-dry cycles. So the main component of hydrophilic coating after 5 wet-dry cycles is silica skeleton and sodium poly-acrylate is considered to have been almost washed away.

Hydrophilicity of the silica film after 5 wet-dry cycles is listed in Table 2. Although the amount of silica film weight are nearly the same with each other (except sample (a)Cr-0), contact angle is dependent upon Cr weight of chromate-phosphate conversion coating and Cr-rich film showed better hydrophilicity. This implies that real surface area of silica film with larger Cr weight of the conversion coating is larger than that with less Cr weight of the conversion coating, because a hydrophilic film with larger real surface area made from identical material corresponds to better hydrophilicity according to Wenzel equation [5].

Figure 4 shows the surface morphology of the silica film after 5 wet-dry cycles and the influence of Cr weight on surface morphology is examined. Roughened surface is observed in each sample, as was the case in the previous report [4], and it is clear that surface morphology of silica film is affected by Cr weight of chromate-phosphate conversion coating. As Cr weight of the conversion coating increases, the substrate of pre-treated aluminum gets less seen through macroporous silica film and the skeleton of silica film gets more continuous rather than fragmented. These types of silica morphology of monolithic silica gel is also known to be created by the gelation reaction of water glass with poly-acrylic acid by acidification, and the morphology of macropores is explained as the frozen transitional structures of phase separation process [6]. As the gelation reaction can be also induced by evaporation [7], it is attempted to explain, by analogy with the above, the mechanism of morphology formation of the silica films in this study, in the later part of this discussion.

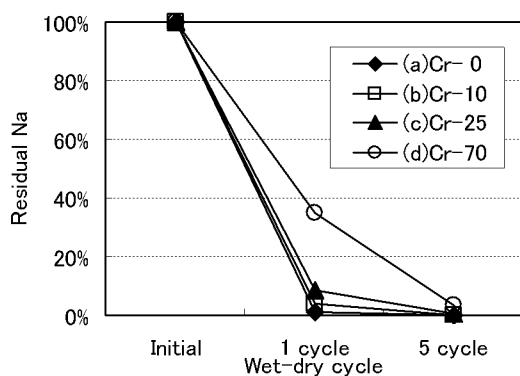


Fig.2 Elution of Na in hydrophilic coating by wet-dry cycle

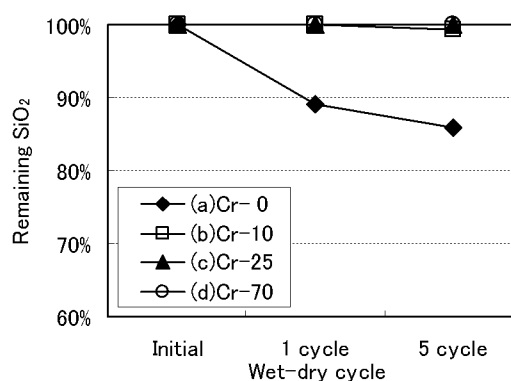


Fig.3 Elution of SiO₂ in hydrophilic coating by wet-dry cycle

Table 2 Contact angle data and remaining film weight of silica film after 5 wet-dry cycles

Sample No.	(a)Cr-0	(b)Cr-10	(c)Cr-25	(d)Cr-70
C.A.(°)	28	14	10	5
Silica film weight (mg/m ²)	232	256	255	255

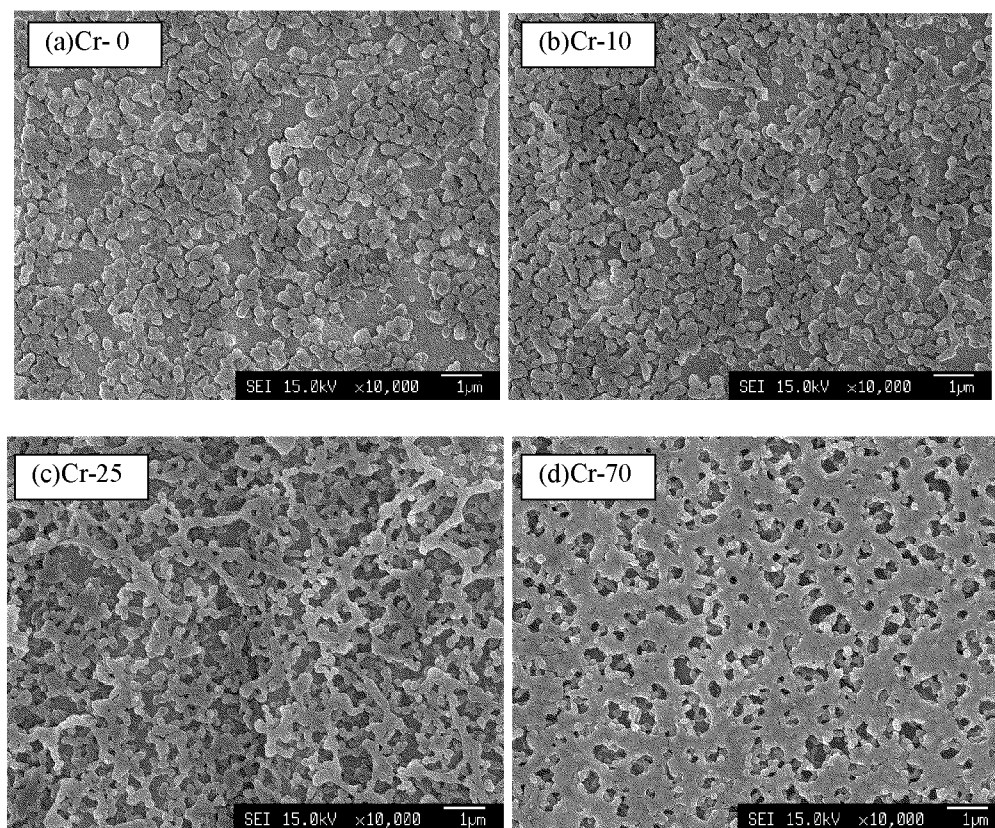


Fig.4 SEM images of silica film after 5 wet-dry cycles

Figure 5 shows the relationship between surface free energy of both polar and dispersion components and Cr weight per unit area of chromate-phosphate conversion coating without hydrophilic coating, which was elucidated by extended Fowkes' equation [8]. It can be seen that the conversion coating with larger Cr weight has higher surface free energy of polar component and lower surface free energy of dispersion component. This implies that chromate-phosphate conversion coating with larger Cr weight interacts more with polar component, i.e., both water glass and sodium poly-acrylate.

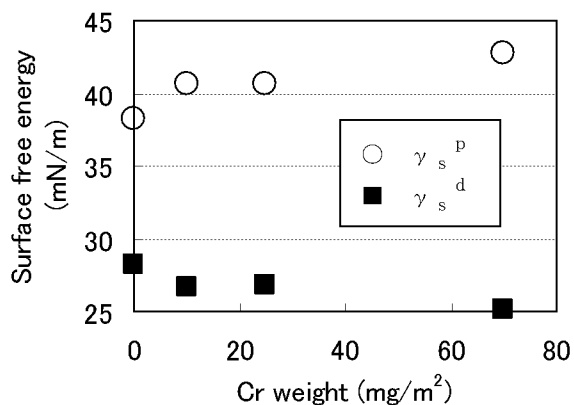


Fig.5 Surface free energy components of chromate-phosphate conversion coating

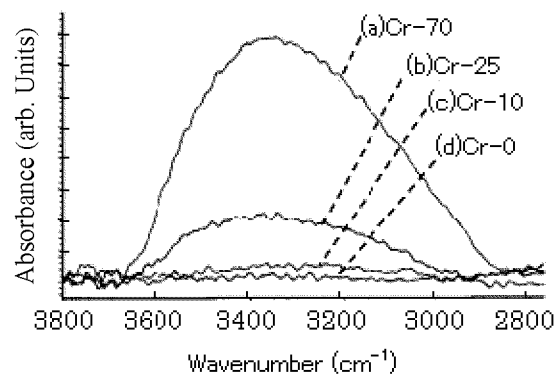


Fig.6 FT-IR spectra of chromate-phosphate conversion coating

Figure 6 shows FT-IR spectra in $2800\text{--}3800\text{ cm}^{-1}$ for each Cr weight of chromate-phosphate conversion coating, without hydrophilic coating. It can be seen that the spectrum of conversion coating with larger Cr weight showed larger absorption peak near $3300\text{--}3400\text{ cm}^{-1}$, which indicates larger amount of hydroxyl group from $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. Existence of abundant polar groups of these hydroxyl and phosphate, which has been reported in the previous paper [3], is considered to lead to larger surface free energy of polar component.

Apart from the present study, roughened morphology of fragmented domain and co-continuous structure made from the mixture of hydrolyzed alkoxysilane or water glass (which is confirmed to have similar polymeric network like hydrolyzed alkoxysilane by ^{29}Si NMR [9]) and poly-acrylic acid with acidifying agents was reported previously for porous monolithic silica-gel synthesis [6] [10]. Phase separation based on the incompatibility between the polymer (i.e., poly-acrylic acid) and siloxane oligomers (i.e., hydrolyzed alkoxysilane or water glass) leads to the formation of micrometer-range heterogeneous structures [11]. This phenomenon was explained as spinodal decomposition, which occurs when stable single phase system is abruptly brought deeply into unstable state by quenching or evaporation etc. so that the fluctuation of the system spontaneously develops with time without requiring any activation energy. The characteristic domain size of resultant silica structure is considered to correspond to a single Fourier component among the various fluctuation wavelengths and it depends upon how abruptly and deeply the original single phase was brought into the unstable state and also upon the mobility of the constituents (i.e., polymer and siloxane oligomers). The fluctuation wavelength is finally frozen by gelation reaction of silica-sol, which is induced by acidification or evaporation of solvent. On the other hand, the self-similar coarsening of the spinodally phase separated domains occurs in order to reduce total interfacial energy between silica-sol and polymer until the gelation reaction completes eventually freezing the evolved fluctuation structure, as is shown in Figure 7 [11].

In our present study, if we assume that the silica film with larger Cr weight of the conversion coating, which has co-continuous structure, correspond to the initial stage of spinodal decomposition, and if we also assume that the silica film with less Cr weight of the conversion coating, which has fragmented domains, corresponds to the later stage of spinodal decomposition with self-similar coarsening, then sufficient Cr weight of the conversion coating stabilized the original single phase, which is made of the aqueous solution of water glass and sodium poly-acrylate, and consequently delayed the evolution of spinodal decomposition with self-similar coarsening. That is, the more stabilized original single phase is not allowed to have enough time for phase separation with self-similar coarsening during the evaporation of solvent water, and the interfacial surface area between silica skeleton and water-soluble conjugate components (i.e., sodium poly-acrylate) is kept large, which then leads to better hydrophilicity of resultant silica skeleton after wet-dry cycles. Similar discussion was reported previously that difference of interaction between a substrate and a binary mixture of polymers on it led to different morphology of film whose mechanism was also explained by spinodal decomposition [12]. Further investigation will verify these assumptions both experimentally and theoretically.



Fig.7 Time evolution of spinodally decomposing isotropic symmetrical system [8]

4. Conclusion

Hydrophilic coating of water glass with sodium poly-acrylate was applied onto the aluminum sheet with pretreatment of chromate-phosphate conversion coating. It was clarified that when Cr content was high, silica film showed better hydrophilicity after wet-dry cycles and the morphology seemed to have more continuous structure rather than fragmented domains. Difference of surface free energy of polar component on the conversion coating without hydrophilic coating was considered to have affected the phase separation of water-glass and sodium poly-acrylate during solvent evaporating process of hydrophilic coating. Morphology of silica films was explained by the mechanism of spinodal decomposition with self-similar coarsening process, which determined the resultant hydrophilicity of silica film.

References

- [1] K. Kamitani, Y. Ota, Y. Mukai, K. Noda, Y. Mukai, K. Hatanaka: J. Japan Inst. Light Metals 50 (2000) 210-215.
- [2] H. Hirasawa: Journal of The Surface Finishing Society of Japan. 57 (2006) 127-132.
- [3] K. Hatanaka, M. Fukui, Y. Mukai, K. Toyose: Kobelco Tech. Rev. 6 (1989) 28-31.
- [4] K. Kamitani, Y. Ohta, Y. Mukai, K. Hatanaka: J. Japan Inst. Light Metals 50 (2000) 147-151.
- [5] R.N. Wenzel: J. Phys. Colloid Chem. 53 (1949) 1466-1467.
- [6] A. Yachi, R. Takahashi, S. Sato, T. Sodesawa, K. Oguma, K. Matsutani, N. Mikami: J. Non-Cryst. Solids 351 (2005) 331-339.
- [7] H. H. Weldes, K. R. Lange: Industrial and Engineering Chemistry 61 (1969) 29-44.
- [8] D.K. Owens, R.C. Wendt: J. Appl. Polym. Sci. 13 (1969) 1741-1747.
- [9] H. Nishino, R. Takahashi, S. Sato, T. Sodesawa: J. Non-Cryst. Solids 333 (2004) 284-290.
- [10] K. Nakanishi, N. Soga: J. Non-Cryst. Solids 139 (1992) 1-13.
- [11] K. Nakanishi: Bull. Chem. Soc. Jpn. 5 (2006) 673-691.
- [12] J. F. Marko: Phys. Rev. E 48 (1993) 2861-2879