Determination of Aluminum Oxide Thickness on the Annealed Surface of 8000 Series Aluminum Foil by Fourier Transform Infrared Spectroscopy

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Abstract

Aluminum foil produced with prescribed thermomechanical processing route develop oxide film. Alloy chemistry and annealing practices, particularly its duration and exposed temperature, determine the characteristics of the oxide film. The magnitude and characteristics of the oxide film may impair surface features leading to serious problems in some applications, such as coating, printing and in some severe cases failure in formability. Therefore, it is important for the rolling industry to be able to monitor the oxide formation on the foil products and quantify its thickness. Well known methods to measure an oxide thickness that is in the order of nanometer, require meticulous sample preparation techniques, long duration for measurements and sophisticated equipment. However, in this study, a simple and rapid grazing angle attenuated total reflectance infrared (GA-ATR-FTIR) spectroscopic method combined with chemometrics multivariate calibration has been developed for the oxide thickness determination which is validated with x-ray photoelectron spectroscopy (XPS). 3000 and 8000 series aluminum foil materials which were produced by twin roll casting technique were used in this study. Foil samples were annealed at various different temperatures and annealing times in a laboratory scale furnace. Immediately after collecting GA-ATR-FTIR spectra, the 3000 series alloy samples were sent to a laboratory where XPS reference oxide thickness measurements had been performed. Partial Least Squares (PLS) method was used to develop a multivariate calibration model based on FTIR spectra and XPS reference oxide thickness values in order to predict the aluminum oxide thickness. The correlation coefficient of XPS reference oxide thickness values versus grazing angle ATR-FTIR based PLS predicted values was found as 0.9903 the standard error of cross validation (SECV) was found to be 0.29 nm in range of 4.9–14.0 nm for Al_2O_3. In addition, the standard error of prediction (SEP) for the validation set was 0.24 nm with the model generated with three principal components (PCs).

Keywords

Twin roll casting • Oxide film • 8000 series aluminum alloy • Fourier transform infrared spectroscopy

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Introduction

With increasing production and consumption amounts, aluminum is the leader in the metallurgy of non-ferrous metals. Development of processes for aluminum and its alloys can be attributed to several of its properties. One of the production techniques of foil and sheet aluminum alloys is twin-roll casting (TRC). This production method has been used for almost 50 years in the aluminum industry. In twin-roll casting, molten metal is fed into two water-cooled rotating rolls, where it solidifies, and then rolled, producing sheet directly from the melt. A wide range of thicknesses and widths can be produced by twin-roll casting [1, 2].

Aluminum sheets with a thickness below 200 µm are described as foils. Coils are cast by utilizing twin roll casting technology (TRC) then subjected to various annealing and rolling practices to obtain foil materials. There are many applications of foils such as: thermal insulations, fin stocks, semi-rigid containers, household foils etc. 8000 series aluminum alloy is one of the typical alloy used for foil productions [3, 4].

Although raw aluminum alloys generally covered with a very thin natural oxide layer, the thickness of oxide layer on the surface of aluminum is tend to grow significantly with increasing temperature [5–7]. One of the steps in the manufacture of aluminum foil is an annealing operation which is used to impart ductility to the foil and to remove lubricants from the surface of the foil. Although it develops an oxide layer on the surface, alloy chemistry, annealing atmosphere, annealing temperature and its duration have significant influence on the composition and characteristics of oxide layer [8]. The thickness of oxide layer formed on aluminum alloy has a significant importance in adhesion and wetting characteristics as well as corrosion resistance [9, 10]. Presence of oxide layer on foil surface creates serious problems for some specific applications of aluminum foils in certain industries such as food packaging where the deep drawing application is critical and brazing applications in industry where wetting characteristic on the aluminum surface directly affect the mechanical bonding and heat transfer systems.

The thickness of end-product is crucial and usually it should be lower than 50 Å, especially for brazing application. To determine accurate measurement of 50 Å or lower thickness of oxide later, more sophisticated techniques are needed. Although sophisticated techniques like x-ray photoelectron (XPS) [11, 12] and transmission electron microscopy (TEM) [13] are suggested in academic area for both determination and characterization of oxide thicknesses, these methods take extended period of time and expensive.

Present study investigates the oxide formation on the surface of aluminum foil for 8000 series alloy produced by industrial annealing practices. A series of samples were prepared from 3000 and 8000 series alloys in a laboratory scale annealing furnace under different annealing parameters (time, temperature) to determine the oxide thickness. In order to develop partial least squares (PLS) chemometrics calibration models, x-ray photoelectron spectroscopy (XPS) were used for the reference analysis of oxide thickness measurements on 3000 series samples. The models generated with 3000 series samples were used to determine oxide thicknesses of 8000 series alloys based on infrared spectroscopic method combined with PLS multivariate calibration.

Experimental Studies

8000 series alloy samples gathered from the final thickness of the production were investigated in order to characterize the surface properties. The alloy is continuously strip cast by an industrial scale twin roll caster. As-cast strip was processed to final foil gauge according to the processing route for producing container foil. The production process consist of homogenization annealing at a certain strip thickness, cold rolling, foil rolling and soft annealing at the final thickness respectively. Chemical composition of the 8000 series alloy is given in Table 1.

To observe the effect of nitrogen and air annealing on the oxide formation, coils were soft annealed under two different atmosphere in an industrial scale furnace. After annealing operation foil samples were investigated by employing scanning electron microscope (SEM). Surface roughness (Ra) of the sample was measured on five different regions of both samples via non-contact optical profilometer.

To determine aluminum oxide thickness which is formed in the nanometer range on the surface of aluminum foil products, FTIR spectroscopy and PLS multivariate calibration approaches are applied on a series of samples prepared under laboratory conditions. Foil samples gathered from the serial production before soft annealing operation, were annealed at 200, 250, 300, 350, 400, 450 and 500 °C for various annealing times (1, 3, 5, 8 h) in air atmosphere.

In order to develop PLS multivariate calibration models, a data set which was gathered from a previous study were

Table 1 Chemical composition of the foil

	Element, wt%				
Alloy	Si	Fe	Cu	Mn	Ti
8000 series	0.16	1.43	0.03	0.63	0.01

used. The data set contains 20 samples of 3000 series alloy of which XPS reference analysis of aluminum oxide (Al_2O_3) had been conducted by Prof. Dr. Şefik SÜZER (Bilkent University, Department of Chemistry). The 20 samples were subjected to five different annealing temperature (300, 350, 400, 450 and 500 °C) and four different annealing time (1, 3, 5 and 8 h). Table 2 shows the reference oxide measurements of these 20 samples.

Grazing Angle Attenuated Total Reflectance (GATR)-FTIR spectra of 20 samples were recorded by using Perkin Elmer Spectrum 100 FTIR Spectrometer coupled with GATR accessory in the wavenumber range of 4000–600 cm^{-1}. The fact that XPS analysis of oxide thickness is quite time consuming and expensive, it was decided to use PLS models generated with 3000 series alloy which composition is similar to 8000 series aluminum alloy foil samples.

Results and Discussion

The macro images of the foil materials which were annealed in two different atmospheres during production are given in Fig. 1. It is clearly seen that the foil surface annealed in air atmosphere looks different from the other one. Foil material annealed in nitrogen atmosphere shows a uniform surface appearance without any visually observable oxidation. However, foil annealed in air atmosphere has white stains at the edges which were formed due to the oxidation during annealing. This heterogeneity on the foil surface leads to different surface tension conditions to appear on the oxidized areas.

To make further studies, oxidized regions were examined via the scanning electron microscope comparatively with the foil having no oxidation (sample on the left in Fig. 1). As seen in Fig. 2, secondary electron images reveal that the oxidation leads to degradation on the foil surface (Fig. 2a, c). The oxidized foil sample surface partially shows micro holes and an uneven surface appearance as compared to the non-oxidized sample (Fig. 2b, d).

The average results of surface roughness measurements show that the oxidized sample and non-oxidized sample exhibit a surface roughness (Ra) values of 0.388 and 0.221, respectively. This observation is consistent with results of SEM images.

Homogeneous distribution and the amount of the lubricant on the foil surface is critical for deep drawing applications [14]. The oxide film formations on the foil surface creates serious problems for some specific applications in which a lubricant is applied and foil is deep drawn to containers. Oxidized surfaces of the foil can affect the proper application of lubricant due to having different roughness profiles and resulting surface tension. Also, surface roughness plays an important role during forming process [15]. An increase in the roughness parameters of the foil may change the friction conditions between die surface and foil. Because of these reasons, the magnitude of oxide layer formed on the foil surface is very crucial for similar applications.

After completing XPS reference analysis studies, multivariate modelling studies were conducted to determine the

Table 2 Al_2O_3 thicknesses of 20 samples belong to 3000 series of aluminum alloys determined by XPS method

Thickness of Al_2O_3 (nm)	Annealing time, h			
Annealing temperature, °C	1 h	3 h	5 h	8 h
300	4.9	5.1	5.3	5.5
350	5.5	5.8	6.2	6.6
400	6.6	7.1	7.4	8.0
450	8.0	9.0	10.0	11.0
500	11.0	12.0	13.0	14.0

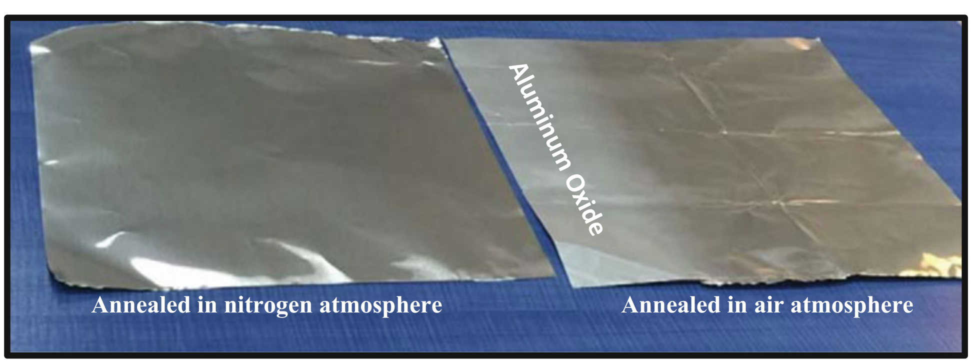

Fig. 1 The macro photographs of the foil materials annealed in two different atmosphere (nitrogen and air)

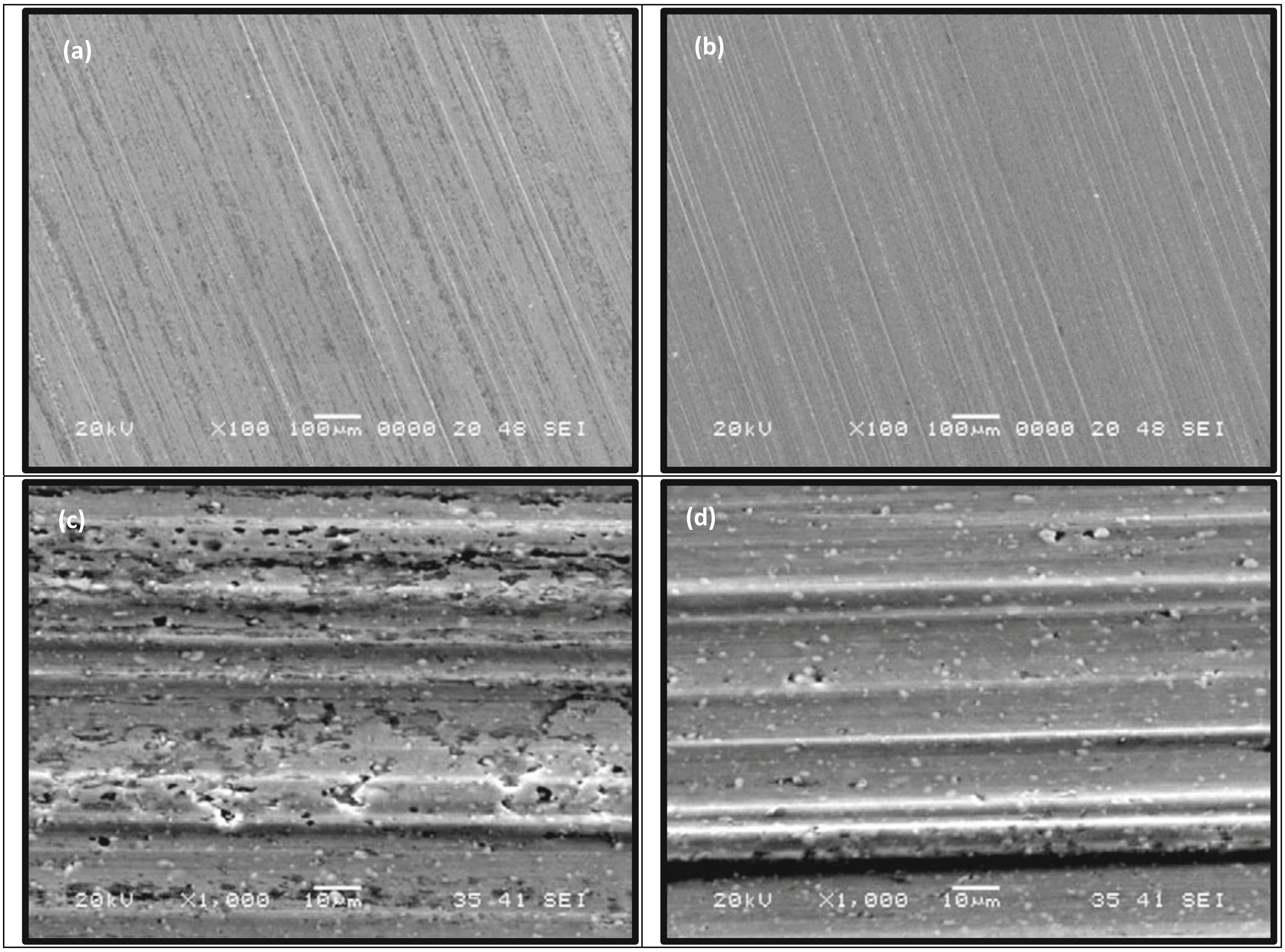

Fig. 2 Secondary electron images of aluminum foil surfaces. **a**, **c** Foil surface annealed in air atmosphere. **b**, **d** Foil surface annealed in nitrogen atmosphere

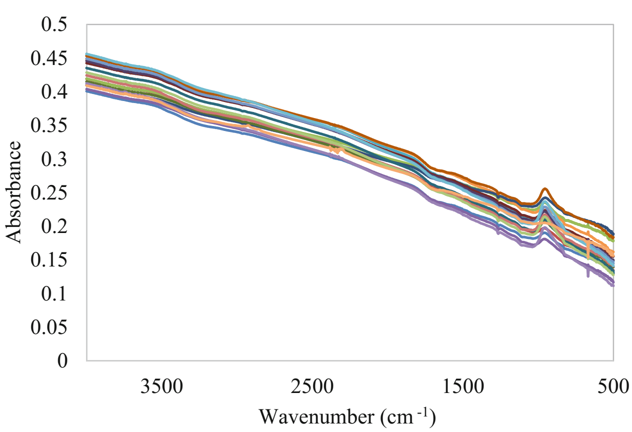

Fig. 3 Grazing Angle ATR-FTIR spectra of the 20 samples from 3000 series alloy

thickness of Al_2O_3 based on FTIR spectroscopy. Figure 3 shows Grazing Angle ATR-FTIR spectra of the 3000 series alloy samples which are given in Table 1.

As can be seen from Fig. 3, raw FTIR spectra of the samples exhibits serious baseline shift problems and therefore spectra must be baseline corrected before further analysis. The fact that the baseline of the spectra shows somewhat nonlinear trend, a second order polynomial baseline function was fitted to each spectrum and this baseline spectrum were then subtracted in order remove baseline offset. Figure 4 shows the baseline corrected FTIR spectra of the 3000 series alloy samples.

As seen from Fig. 4, after baseline correction, absorbance peak around 950 cm^{-1} was become apparent in relation to the reference oxide thickness values given in Table 2. At this point, one might consider using a simple least squares approach to develop calibration model for the oxide thickness. However, the spectra have some shift on the wavenumber scale at the peak maxima and this cause deviation from linearity at the peak maxima. Partial least squares (PLS) is well known factor based calibration method which is used for complex multivariate problems [16–18]. A modified version of the PLS algorithm which was implemented in MATLAB Programming environment was used to develop multivariate calibration model for the Al_2O_3 thickness determination from FTIR spectra. For this, 17 samples from Table 2 were used to construct calibration set and the remaining 3 samples were used to construct independent validation set for 3000 series aluminium alloy. Modelling is done with a leave-one-out cross validation in the calibration set and the model was also tested with the independent validation set. Figure 5 shows reference vs. predicted plot of Al_2O_3 thickness.

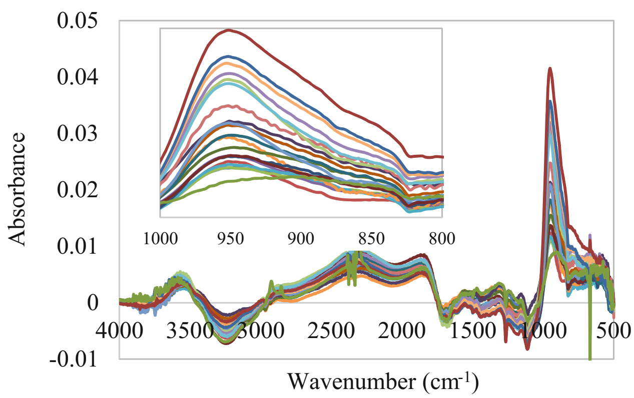

Fig. 4 Baseline corrected Grazing Angle ATR-FTIR spectra of the 3000 series alloy samples

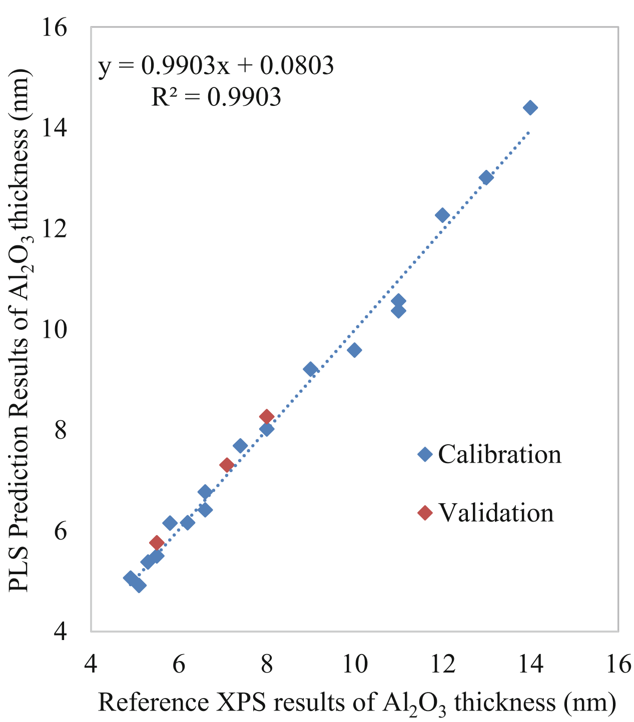

Fig. 5 Reference versus predicted plot of Al_2O_3 thickness by using PLS method

With the use of the PLS multivariate calibration method quite successful model was developed for the Al_2O_3 thickness determination based on Grazing Angle ATR-FTIR spectroscopy without tedious and time consuming reference XPS analysis. As seen from Fig. 5, the correlation coefficient of the reference oxide thickness values vs. PLS predicted values was around 0.99 and the standard error of cross validation (SECV) was found to be 0.29 nm in an interval of 4.0–16.0 nm. In addition, the standard error of prediction (SEP) for the validation set was 0.24 nm with the model generated with three principal components (PCs).

In order to test the predictive performance of the PLS multivariate calibration model for the Al_2O_3 thickness determination, a total of 28 samples of 8000 series of aluminium alloy which were annealed at seven different temperature (200, 250, 300, 350, 400, 450 and 500 °C) and four different annealing times (1, 3, 5, 8 h) in air were used. Figure 6 shows the baseline corrected Grazing Angle ATR-FTIR spectra of the 28 samples annealed in air atmosphere from 8000 series alloy.

When compared with the Fig. 4 which gives the 3000 series alloy baseline corrected FTIR spectra, the 8000 series alloy baseline corrected FTIR spectra shows some difference. However, the general appearance of the main absorbance peak around 950 cm^{-1} corresponding Al_2O_3 is quite similar in both Figs. 4 and 6. This similarity in FTIR spectra of both 3000 and 8000 series alloys makes it possible to use the PLS model generated with 3000 series samples in the prediction of oxide thickness of the 8000 series alloy samples. Table 3 shows the predicted Al_2O_3 thickness of 8000 series alloy annealed in air atmosphere. As seen from Table 3, annealing atmosphere at various temperature and time settings generated aluminium oxide thickness values ranging from 4.23 to 14.36 nm. Although the Al_2O_3 thickness prediction values given in Table 3 are in good agreement with the XPS reference analysis of the 3000 series

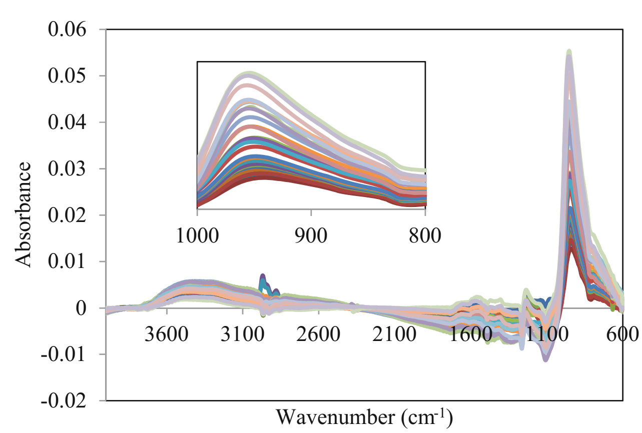

Fig. 6 Baseline corrected Grazing Angle ATR-FTIR spectra of the 8000 series alloy samples annealed in air atmosphere

Table 3 PLS predicted Al_2O_3 thickness of 8000 series alloy annealed in air atmosphere

Annealing time (h)	Annealing temperature						
	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C
1	4.26	4.79	5.59	6.43	8.01	12.57	13.15
3	4.23	5.31	5.87	7.39	9.81	12.78	14.36
5	4.61	4.89	5.93	8.31	11.47	12.42	14.18
8	4.78	5.38	6.48	8.39	9.58	11.88	14.05

alloy samples, future studies should be done to further validate and improve the method, since only 3000 series Al alloy samples were used for model construction and validation.

Conclusions

An increase in the surface roughness of the foil creates serious problems for some specific applications such as deep drawing of the foil, lacquering and printing. Annealing in air atmosphere can cause oxidation on the foil surface and increases surface roughness of the material. However, the results demonstrated that oxide thickness is greatly affected by annealing temperature rather than annealing time. On the other hand, annealing in nitrogen atmosphere is expected to protect material surface from the air oxidation as seen from production sample surfaces shown in Figs. 1 and 2. However, pilot scale nitrogen atmosphere annealing is currently under study and the results will be presented in a further report.

Successful PLS multivariate calibration model was developed for the Al_2O_3 thickness determination based on Grazing Angle ATR-FTIR spectroscopy. Determination of aluminum oxide thickness on the annealed surface of 8000 series aluminum foil by Fourier transform infrared spectroscopy coupled with PLS multivariate calibration model reveals that aluminium oxide thickness values are found to be ranging from 4.23 to 14.36 nm.

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