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OXIDATION OF ALUMINUM FOIL UNDER SIMULATED HIGH TEMPERATURE ANNEALING USING THERMOGRAVIMETRY

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The oxidation rate of commercial aluminum foil (0.002 inches in thickness) was followed in air using a thermogravimetric analyzer as a simulated micro annealing oven. Rate constants were calculated for a parabolic rate law fit from 0.5 to 1.5 hours at temperatures from 510 to 630°. The maximum weight gain of 27 μg/cm was found at 621° in air. An unusual adsorption at 93° was observed in several atmospheres while bringing the sample up to isothermal temperature and was related to surface contamination collected during rolling. The results were compared to those for pure aluminum and found to be similar.

The oxidation rate of pure aluminum surfaces at elevated temperatures in the presence of dry and moist oxygen has been studied extensively and the rate of reaction between water vapor and aluminum was found to be greater than that between the metal and oxygen; blister formation was also found to occur in the presence of water vapor [1].

The study of the kinetics of oxidation has shown that the rate of oxidation does not follow either a parabolic rate law or a direct logarithmic law [2, 3]. This was explained by the fact that the formation of γ-alumina crystallites, which nucleate beneath the initial amorphous oxide film, are assumed to achieve a terminal thickness rapidly followed by radial growth. This growth proceeds at a constant velocity until the crystallites impinge on one another.

A few experiments have been carried out on commercial 5052 aluminum-magnesium alloys and the rate was found to be much faster than for high-purity aluminum and proceeded to much higher weight gains [4]. Electron diffraction examinations of oxidized specimens showed formation of magnesium oxide on the alloy. Oxidation rate was also shown to be a function of surface roughness. The highly polished and smoother surfaces were oxidized at a much lower rate.

Little has been reported on the air oxidation of "as rolled" aluminum foil or under conditions present in commercial rolling processes.

The present study employed the use of a thermogravimetric analyzer (TGA) as a micro annealing oven to study oxidation rates of commercial "as rolled" aluminum foil under various conditions simulating the high temperature annealing process, referred to as homogenization.

Experimental

Sample history

The foil samples utilized in this investigation were prepared from continuous cast 1100 alloy by rolling to gauge on commercial equipment at R. J. R. Archer Inc. The fabrication schedule included two rolling passes from the continuous cast reroll gauge of approximately 0.25″ to the intermediate anneal point followed by four or five rolling mill passes to the finished gauge of 0.0034″, 0.002″ and 0.0014″.

The foil at this point was in the −H18 temper (full-hard) and was covered with a very light, residual film of a foil rolling formulation consisting of a petroleum base oil fortified with a fatty acid and a fatty ester. The foil surfaces were bright and smooth.

The chemical composition of the stock from which these foils were produced had typical values noted below.

% Si	% Fe	% Cu	% Mn	% Zn	% Ti	% B	% Al
0.12	0.45	0.08	0.015	0	0.012	0.002	Balance

Apparatus and procedure

The DuPont 950 TGA with a platinum pan and quartz envelope was calibrated to record 0.4 mg/inch with an accuracy of 0.005 mg. Dynamic atmospheres of purified air, high purity nitrogen, and helium were used at flow rates of 300 ml/min. Vacuum operation was carried out with a two-stage mechanical pump.

Approximately 100 mg samples of aluminum foil, 0.002, 0.0014 and 0.0034 inches in thickness, and measuring about 0.25 by 5.75 in. (a geometric area of 9.3 cm^2) were rolled into tight cylinders in order to simulate rolled foil. The samples were purged for about 15 min. prior to heating, then brought up to the desired isothermal temperature in exactly 8 min. The weight of the sample was then recorded as a function of time for about 3 hours. All but 0.5 mg of the sample was electronically suppressed so that the maximum sensitivity could be used.

The data were handled in three ways: (1) A plot of percent oxidation with respect to time was found to initially follow a parabolic law and then followed an almost linear relationship. (2) This was confirmed by a plot of percent oxidation squared with respect to time which followed a linear relationship for only the first part of the curve. A rate constant based on weight with the units % oxidation/hr. was obtained from those data. (3) Similar results were obtained on an area basis for a plot of (mg/cm^2)^2 with respect to time. A rate constant with the units cm^2/hr. was obtained from that data using the geometric area of 9.3 cm^2.

Temperature dependency of oxidation rate

The effect of temperature on the oxidation rate of 0.002 in. foil in air was determined and results are given in Table 1. There was an almost exponential increase in the rate from 510 to 586° followed by an apparent decrease and a second maxi-

Table 1

The effect of temperature on the oxidation rate of aluminum foil in air

T, °C	% Wgt. gain (3 hrs.)	% Ox./hr. X 10^3	Cm²/hr.
510	0.029	0.04	1.5
538	0.054	1.2	11
566	0.172	4.5	67
586	0.186	16.3	215
605	0.130	1.9	26
613	0.094	1.3	40
617	0.162	—*	—*
621	0.256	9.9	127
630	0.170	5.0	65

* no value available

mum at 621°. There was considerable overlapping in the data as shown in Fig. 1. The parabolic plots are not shown but the rate constants given in Table 1 were determined from the slope of the line obtained between 0.5 and 1.5 hours. The percentage oxidation at 3 hours as a function of temperature is given in Fig. 2. Above 638° the samples began to sinter and melt.

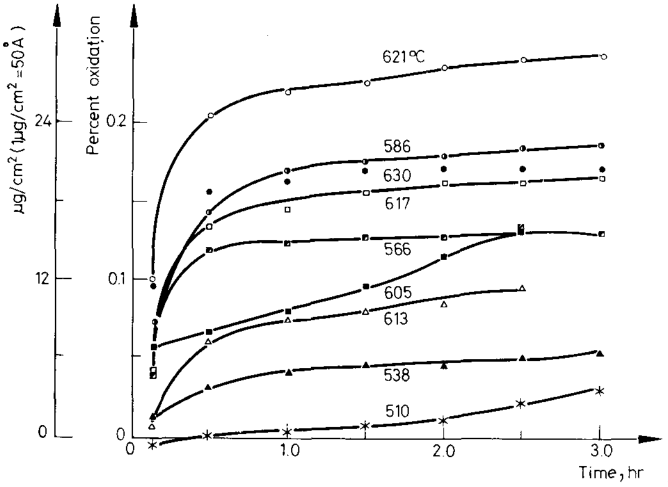

Fig. 1. Temperature dependency of oxidation rate of aluminum foil; 0.002 inch foil in air

Effect of atmosphere on oxidation rate

The rate of oxidation of aluminum foil of varying thickness in air, nitrogen and helium atmospheres was determined at 621° as shown in Table 2. Figs 3, 4 and 5 depict typical rate curves for 0.002 in. foil. The data were consistent and revealed significant oxidation for foils of all three thicknesses in nitrogen and helium.

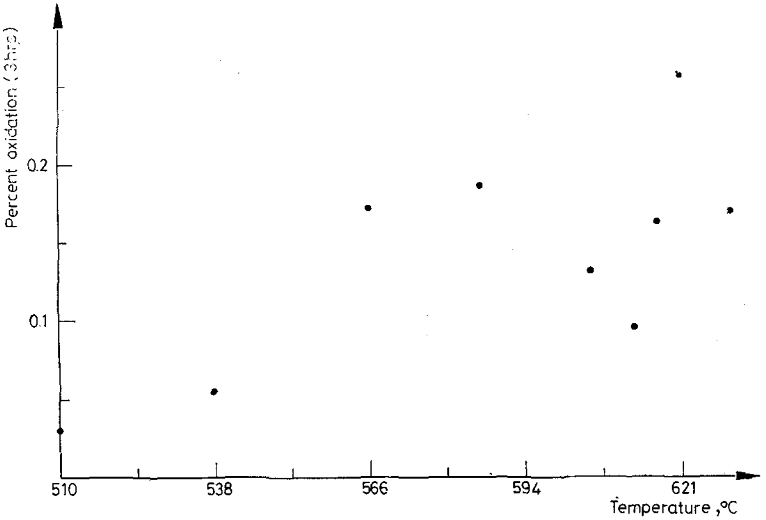

Fig. 2. Temperature dependency of oxidation rate of aluminum foil; 0.002 inch foil in air

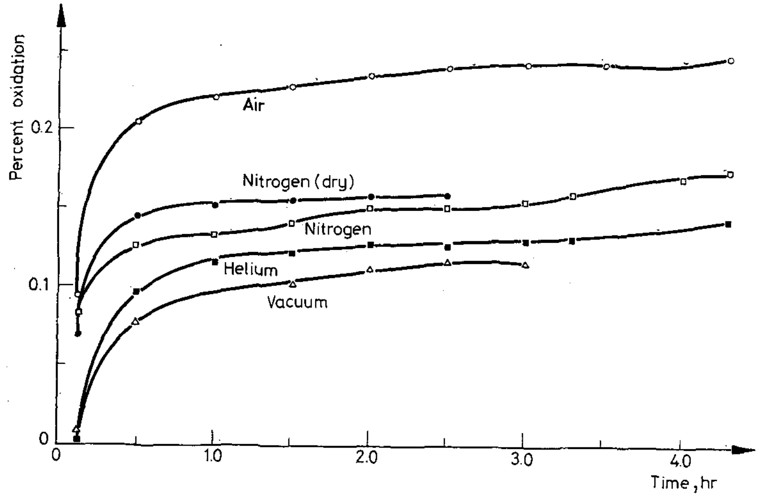

Fig. 3. The effect of atmosphere on the percent oxidation of aluminum foil; 0.002 inch foil in air at 621°

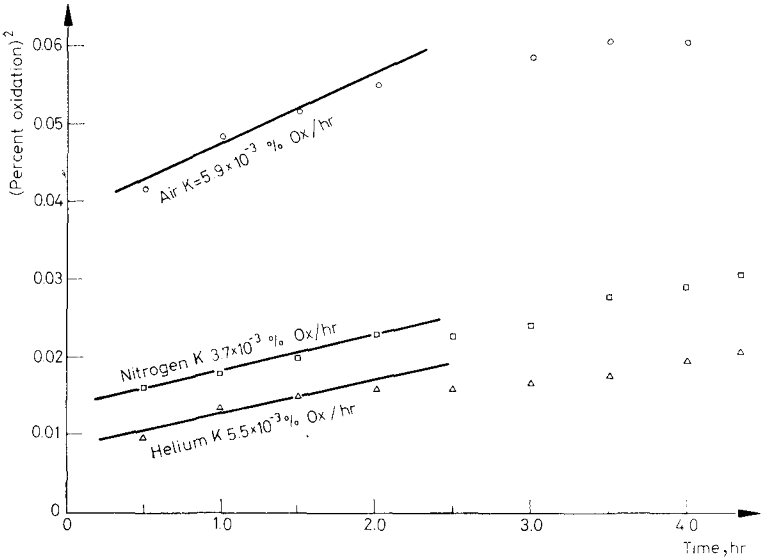

Fig. 4. The effect of atmosphere on the oxidation rate (weight basis) of aluminum foil; 0.002 inch foil in air at 621°

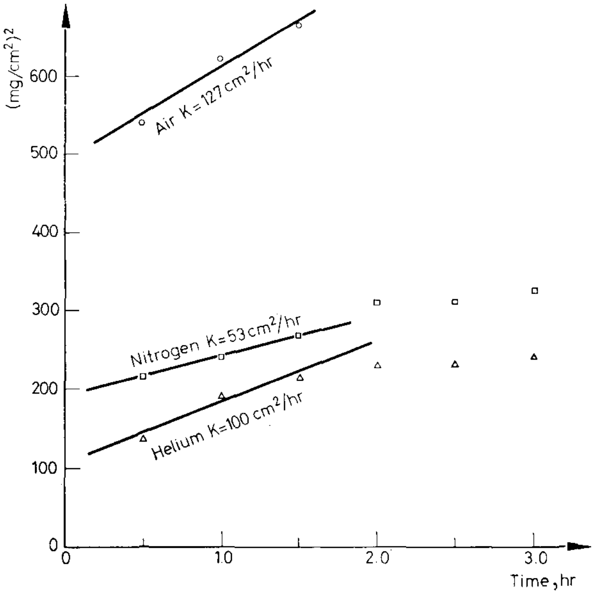

Fig. 5. The effect of atmosphere on the oxidation rate (area basis) of aluminum foil 0.002 inch foil in air at 621°

Table 2

The effect of atmosphere on the oxidation rate of aluminum foil of different thickness at 621°

Thickness, in.	Atmosphere	% Wgt. gain	% Ox/hr. X10^3	cm^2/hr.
0.0014	Air	0.192		
0.0014	N_2	0.179		
0.0014	He	0.112		
0.002	Air	0.256	9.9	127
0.002	N_2	0.155	3.7	53
0.002	He	0.144	5.5	100
0.002	Vacuum	0.115	4.4	63
0.002	N_2 (dry)	0.159	3.3	46
0.0034	Air	0.188		
0.0034	N_2	0.145		
0.0034	He	0.036		

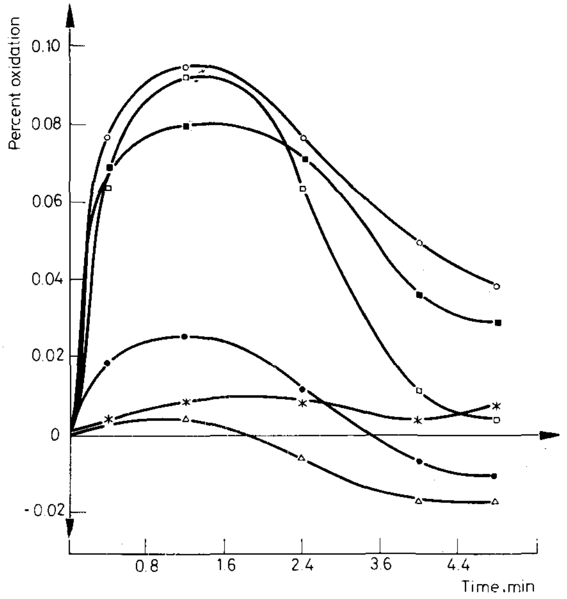

Fig. 6. Effect of atmosphere on the initial oxidation rate of aluminum foil; 0.002 inch foil from ambient to 621°; ○ air; ■ nitrogen (dried); * helium (extracted in acetone); □ nitrogen; ● vacuum; △ helium

To determine if excess moisture in the nitrogen was responsible for the greater rate the gas was passed over a 5 Å molecular sieve column. The oxidation rate of 0.002 in. foil under this dry nitrogen is shown in Table 2. There was no apparent difference in comparison with the standard nitrogen determination.

The use of vacuum with a 2-stage mechanical pump indicated the oxidation rate of 0.002 in. foil to be less than that in nitrogen and helium but with an unusually large weight gain indicating the non vacuum tight conditions. The pressure was not measured.

It was observed in all atmospheres that there was an apparent plateau in the weight gain curve which occurred at different times under each atmosphere in no regular manner. This plateau generally occurred later in time for samples in air as shown in Fig. 3. In atmospheres other than air there was another weight gain after the plateau. Determinations to six hours in air showed very little, if any, weight gain after four hours.

Miscellaneous reactions of aluminum foil

It was observed that during the heating of samples up to the isothermal temperature of interest, represented by the first 5 minutes, there was a weight gain with a maximum at approximately 93°. These results are given in Fig. 6 for several samples of 0.002 in. foil in different atmospheres. The weight gain was greatest in air and nitrogen and approached 0.10% by weight. In helium, however, there was only a 0.004% weight gain followed by a loss of approximately 0.02%. A sample that had been refluxed for 24 hours in acetone and examined in helium exhibited a slightly larger weight gain with no subsequent weight loss. A determination under vacuum resulted in an intermediate weight gain followed by a loss approaching that in helium.

Surface area measurements

Surface area measurements were made on several 2 g samples of 0.002 in. foil using a Numino-Orr Surface Area Analyzer with krypton adsorption. The data revealed no difference in area between an oxidized sample and an unoxidized sample and was estimated to be about 2–4 M^2/g.

Discussion

The oxidation rates found for the aluminum alloy under study agree favorably in general terms with those found in the literature. However, it should be emphasized that with the exception of the work by Cochran and Sleppy [5] the bulk of the literature data are concerned with pure aluminum of known roughness. No data on surface roughness was available in this work. There was also no measure of the amount of initial oxide film.

The magnitude of the weight gain, 15 – 27 μg/cm^2, was in the range found for 5052 aluminum-magnesium alloy by Cochran and Sleppy. This represented a thickness of 750 – 1350 Å. They also found that the rate approached a parabolic rate law. The present rate data followed a parabolic law to about 1.5 hours for most samples then a short period of no oxidation and finally followed an almost linear law. Gulbransen and Wysong [4] found a parabolic rate from 350° to 475° and a linear rate above this temperature region for the oxidation of pure aluminum with oxygen. All the present data were determined above 475° and did not support these results. It is obvious that the kinetics are complex.

The experimental procedure used in this study greatly accelerated the rate and therefore shortened the time necessary to reach maximum oxide formation. It was this weight gain, measured as percentage oxidation because of lack of accurate surface area data, rather than the calculated rate constants, that provided comparative rate data.

It was shown that in most cases the oxidation reached a maximum in about 3 hours because of rapid heat transfer in a micro furnace. It is reasonable to assume that this maximum oxidation is comparable to the eight hour period in plant operation where heat transfer is the limiting factor. It is primarily this maximum oxidation that will be used in the discussion to follow.

Temperature dependency of oxidation rate

The shapes of the temperature dependency curves shown in Fig. 1, including some overlapping, were not unusual and similar curves were reported for the 5052 alloy mentioned above. It is clear that the oxidation rate of aluminum foil is a function of temperature. The rate below 538° was found to be only about 80% that at 621°. There is no clear explanation for the anomalous results obtained between 566 – 630°. Similar results have been found both for pure aluminum and 5052 alloy. The apparent minimum near 613° was more severe than those previously reported but may be related to a barrier thickness that would cause a reduction in oxidizing area. The maximum oxidation was found at the temperature of plant operation, 621°.

The effect of atmosphere on the oxidation rate

It is clear that the atmosphere during homogenization is critical. The use of nitrogen and helium resulted in considerable reduction in the oxidation rate of foils of three different thicknesses. There was no apparent explanation for the consistently higher rate for nitrogen compared to helium. The use of dried nitrogen gave the same results so that the presence of additional moisture in the nitrogen was discounted. The residual oxygen value should have been similar for both nitrogen and helium.

The random effect of thickness on oxidation rate may be related to possible differences in surface properties of the three samples.

Miscellaneous reactions of aluminum foil

The TG data at low temperature, 93°, indicated a significant weight gain for aluminum foil in both air and nitrogen atmospheres which is attributed to adsorption of oxygen or nitrogen on the organic film surface. The determination in helium with no appreciable weight gain supports this view. The subsequent weight loss in helium was a measure of the organic film with a value of about 0.02%. Reflux of a similar sample in acetone followed by determination in helium resulted in no weight loss which substantiated the fact that the acetone extractable organic film was responsible for the adsorption. It should also be emphasized that the desorption curves were all similar in shape. It did not seem likely that nitrogen was being retained by the organic film, but the data do not preclude this possibility. The significance of these results is open for discussion.

Conclusions

It is concluded that TG is a convenient method for the study of oxidation kinetics of aluminum foil. Commercial "as rolled" aluminum foil was found to react with oxygen to form a crystalline oxide layer of a maximum thickness of about 1300 – 1400 Å. The mechanism of reaction was found to be complex as the kinetic data failed to fit theoretical curves, but the results were similar to those reported for pure aluminum. The degree of oxidation during annealing can be controlled by proper selection of temperature and atmosphere.

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Résumé — La vitesse de l'oxydation dans l'air de feuilles d'aluminium commerciales (épaisseur 0.002") a été suivie à l'aide d'un dispositif thermogravimétrique pour simuler un micro-four de recuit. On a calculé les constantes de vitesse en ajustant les données sur une loi parabolique, de 0.5 à 1.5 heures, à des températures de 510 à 630°C. On a trouvé que dans l'air, le gain de masse maximal s'élève à 27 μg/cm^2 à 621°C. On a observé, à 93°C et dans diverses atmosphères, une adsorption insolite pendant le chauffage de l'échantillon jusqu'à la température de l'isotherme. Ce phénomène a été rattaché à une contamination superficielle pendant le laminage. Les résultats comparés à ceux obtenus avec l'aluminium pur apparaissent similaires.

ZUSAMMENFASSUNG — Die Oxydationsgeschwindigkeit von handelsüblicher Aluminiumfolie (0.002″ Stärke) in Luft wurde in einem thermogravimetrischen Analysator als simulierten Mikro-Temper-Ofens verfolgt. Die Geschwindigkeitskonstanten wurden für eine parabolische Anpassungsgesetzmässigkeit zwischen 0.5 und 1.5 Stunden bei Temperaturen von 510 bis 630° berechnet. Das Maximum der Gewichtszunahme, 27 μg/cm, wurde in Luft bei 621° gefunden. Eine ungewöhnliche Adsorption wurde in verschiedenen Atmosphären bei 93° beobachtet, während das Muster auf die isotherme Temperatur gebracht wurde. Die Erscheinung wurde mit einer beim Walzen auftretenden Oberflächenkontamination in Zusammenhang gebracht. Die Ergebnisse wurden mit den bei reinem Aluminium gefundenen verglichen und ähnlich gefunden.

Резюме — Измерена скорость окисления промышленной алюминиевой фольгт (толщина 0.002 дюйма) в воздухе с использованием в качестве микропечи термогравиметрического анализера. Константы скорости расчитаны по параболическому правилу скорости от 0.5 до 1.5 часов при температурах от 510 до 630°. Наибольшое увеличение веса (27 μг/см) обнаружено в воздухе при 621°. В некоторых средах наблюдалась необычная адсорбция при 93° в ходе достижения изотермической температуры образца, что отношено к загрязнению поверхности во время прокатки. Результаты, полученные для чистого алюминия аналогичны.