Tribological Properties at the Interface of the Aluminum and Aluminum Oxide

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***Abstract*—This paper presents the tribological behavior of aluminum/aluminum interaction. The effect of passive oxide film prepared by different methods such as thermal oxidation, chemical oxidation and chemical oxidation followed by annealing on the coefficient of friction is experimentally determined using a pin on disk tribometer. The experiment showed that, for the given sample, the pure aluminum/aluminum interaction had a mean coefficient of friction of 0.55. Thermal oxidation and chemical oxidation reduced the friction coefficient. Chemically oxidized sample produced amorphous film and when annealed, the film recrystallized to form γ-alumina. The coefficient of friction value of the recrystallized oxide film increased to 0.61. An XRD pattern showed existence of γ-alumina for annealed and chemically oxidized sample. No significant peaks were seen on the XRD pattern for chemically oxidized sample confirming the amorphous nature. The films prepared by all the above methods were brittle and wore off fast.**

Keywords—XRD; Phases; Wear Tracks; Oxidation Enthalpy; Coefficient of Friction

I. INTRODUCTION

Aluminum is one of the most heavily used metal in mechanical industries due to its light weight and high specific strength. Unlike iron, aluminum forms a passive oxide film on the surface which protects it from further oxidation. The study on mechanical and tribological interactions between aluminum/aluminum is of great interest to the automobile industry as aluminum alloys are now considered as a substitute for steel to reduce payload because of their high specific strengths.

Aluminum oxide film on aluminum substrate is widely used in MEMS (Micro Electro-Mechanical Systems) as the dielectric coating because of its high thermal stability [1], low conductivity [1], and high permittivity [2] along with large band gap [3]. Understanding the frictional behavior of these oxide film on aluminum substrate is important to predict the life of these coatings. Aluminum oxide is also biocompatible and hence has been used extensively as a coating on aluminum and titanium prosthetics [4].

The fabrication of aluminum oxide films on different substrates is much easier compared with other materials. Especially on aluminum, a passive oxide film is always formed at atmospheric condition. Thickness of this film can be increased by thermal oxidation. A controlled porous film growth, with doping, can be manufactured on different substrates by anodic oxidation [5-6]. Understanding the tribological and mechanical properties of these oxide films is necessary to predict the suitability and functional duration in different applications.

Properties of the film and interface are greatly influenced by fabrication process. A porous oxide film with good symmetry can be obtained by anodic oxidation. On the other hand, structure and thickness of the film formed by thermal oxidation depend heavily on oxidation temperature and time. At low temperature (T < 400 ^{0}C), an amorphous phase of aluminum oxide thin film can be obtained within a shorter time (< 60 s). But, with high temperature a crystalline phase of aluminum oxide thin film can be obtained. The thickness and growth rate are highly dependent on temperature. A very thin layer of oxide film (1~2 nm thick) can be obtained by reaction of aluminum in an oxalic acidic solution (chemical oxidation). Sputtering is also a good method to produce uniform coating. The thickness of the film can be increased by increasing the sputtering time.

Hiratsuka et.al. reported that oxidation enthalpy or heat of oxide formation has an influence on the friction coefficient between two metals [7]. In vacuum the coefficient of friction increases with oxidation enthalpy whereas in the presence of oxygen it has the opposite effect. The standard formation energy of aluminum oxide from aluminum is 1676.8 $KJmol^{-1}$, which is much higher than metals like platinum, silver, copper, iron and magnesium. The coefficient of friction of alumina/aluminum interface is high in vacuum and low in oxygen. It has also been reported that there exists strong adhesive forces between alumina and aluminum both in vacuum and in atmospheric oxygen [7]. The presence of moisture in the atmosphere also influences the friction and wear of the aluminum and its oxide.

Understanding the tribological properties of aluminum oxide layer is very important, as most surface coating applications involve sliding and Nano-indentation[8]. In the present study, the coefficient of friction of aluminum oxide layer was prepared by two methods: thermal oxidation, chemical oxidation with oxalic acid. The coefficient of friction for the oxide film prepared by the above two method is experimentally determined using a custom-made pin on disk tribometer. The coefficient of friction of pure aluminum/aluminum interactions and wear characteristics of the oxide film are also determined. The effect of annealing on the properties, growth and recrystallization of these films is also analyzed.

II. EXPERIMENTAL PROCEDURE

A. *Substrate Preparation*

The experiment was conducted using AA 1100 as it is commonly used in general fabrication and metal spinning. Aluminum alloy 1100 has a composition of 99.88% Al, 0.1% Cu and 0.02% other. Prior to deposition, the substrates were cut into appropriate dimensions (8 cm x 8 cm, thickness 0.8 mm) and polished to remove any surface cracks. It was then cleaned with soap and water to remove grease and dirt. The substrates were then sonicated in a mixture of acetone, isopropanol alcohol and distilled water for removing surface contaminations.

B. *Film Preparation*

Aluminum metal substrate was oxidized at 80 ^{0}C for 1 hour in 0.16 M aqueous solution of oxalic acid. The sample was then annealed at 400 ^{0}C for 3 hours. We expected to enhance the crystallinity of aluminum oxide films produced by chemical treatment. An amorphous hydrated film consisting of different phases of aluminum oxide, was prepared by this method. Also, a bare aluminum substrate was annealed at 400 ^{0}C for 3 hours in the air to produce a thin oxide layer.

C. *Film Characterization*

The X-ray diffraction (XRD) measurements were conducted with a Cu Kα (λ=1.5418 A˚) radiation (PANalytical X'Pert Pro MPD) to determine the crystal structure of both Al substrate and aluminum oxide films. The scan range was maintained from 20° to 70°.

D. *Pin on Disk Tribometer*

The tribology tests were conducted on a custom-made pin- on disk tribometer. It consisted of a cantilever with a pin attached at the end. The pin had provision to add different magnitudes of weight so that data could be collected at different loads. Two strain gauges were attached to the lateral faces of the cantilever to measure the deflections. The test specimen was screwed to a rotating platform and rotated at constant speed. Once the platform reached steady rotation speed, the pin with normal weight was placed carefully so that the initial interaction of the pin and the film could be measured with the least amount of error. Since the films were only nanometers thick, the initial interaction between the surfaces were made so that the wear on the film due to impact was minimal.

Due to friction, a lateral force would be exerted on the cantilever which deflects the strain gauges. The inner strain gauges underwent compression, whereas the outer one was subjected to tension. The piezoelectric property of these gauges gave rise to a differential voltage, which was collected via a data acquisition system and was interfaced to a computer running custom LabVIEW software. Real-time deflection and frictional force data were collected and saved for further analysis. The forces acting on the substrate is shown in Fig. 1.

The surface roughness of the pin used was 110 nm. The pressure exerted on the film by the pin on the film is calculated by measuring the thickness of the wear tracks using an optical microscope. Speeds of 120 rpm, 200 rpm were used for all data collection. All the readings were recorded at room temperature and ambient air-conditions (1 atm.).

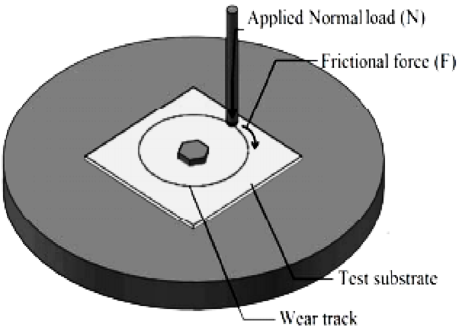

Fig.1. Pin -on disk tribomete [9]

III. . RESULTS AND DISCUSSION

A. *Friction Coefficient of Pure Aluminum*

It has been established that a strong interactive force exist between aluminum and aluminum during rubbing [7]. The coefficient of friction greatly depends on the alloying elements of the interacting aluminum parts. A wide range of friction values, sometimes greater than unity, had been established for aluminum and aluminum interaction depending on composition, environment, lubrication and other factors [10-12].

Since aluminum can be easily oxidized, a passive oxide films is always present on the aluminum surface at atmospheric conditions. To have pure metal to metal contact, the experiment was run for a greater number of cycles so that the oxide film would be eroded. The tests were run at 120 rpm and 200 rpm. The results from 200 to 250 s after the test start time were plotted in Fig. 2 (a) and (b). The analysis showed that pure aluminum/aluminum interaction had a mean coefficient of friction 0.55.

The strong interaction forces between aluminum surfaces [7] were also confirmed from the analysis of wear tracks. The pin also underwent considerable wear and had to be re polished. Wear tracks and optical microscope pictures at 80x magnification are shown in Fig. 3 and Fig. 4.

It was observed that the width of the wear track increased with increase in speed and load. However, when the speed was increased at a specific load, the normal pressure exerted by the pin on the disk decreased. This gave conclusive evidence that aluminum/aluminum interaction depended on the relative velocity of sliding. As the sliding velocity is increased wear also increased.

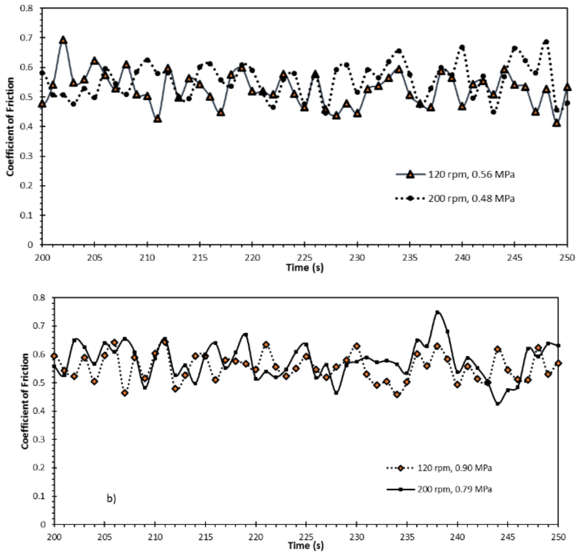

Fig. 2. Coefficient of friction values for pure aluminum / aluminum interactions at different speeds and pressure: (a) 120 rpm/0.56 MPa and 200 rpm/0.48 MPa; and (b) 120 rpm/0.90 MPa and 200 rpm/0.79 MPa.

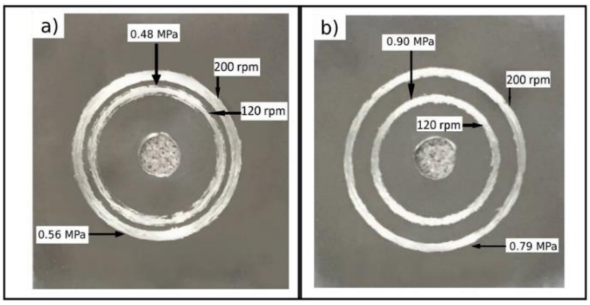

Fig. 3. Wear tracks for pure aluminum/ aluminum interaction: a) 120 rpm/0.56 MPa and 200 rpm/ 0.48MPa, and b) 120 rpm/0.90 MPa and 200rpm/0.79 MPa.

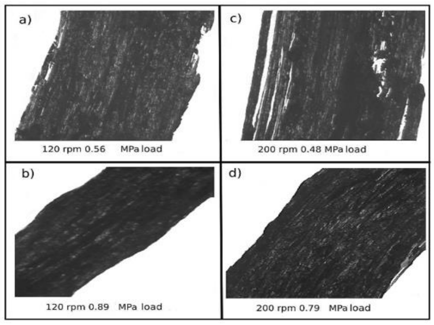

Fig. 4. Optical microscope photographs of wear tracks of pure aluminum/aluminum interaction at 80x magnification: (a) 120 rpm/0.56 MPa; (b) 120 rpm/ 0.89 MPa; (c) 200 rpm/0.48 MPa; and (d) 200 rpm/0.79 MPa.

B. Annealed Aluminum Friction Coefficient

The effect of annealing (thermal oxidation) temperature on the formation, structure, and thickness of the oxide film has been studied extensively. The fi a) wth rate, amorphous/crystalline nature of the fi d saturation film thickness are a function of temperature. At higher temperature the kinetic energy of the oxygen atoms in the atmosphere increases and the number of oxygen atoms sticking (sticking probability) to the aluminum substrate also increases and aids in oxidation. However, it has been reported that at elevated temperature (around 500 ^{0}C) the initial film growth rate decreases as high kinetic energy of oxygen atoms reduces the sticking to the surface (sticking probability decreases) [12]. An oxygen rich amorphous oxide film is formed at lower temperature whereas, an aluminum rich film is formed at elevated temperature. A stoichiometric aluminum oxide (γ-Alumina) film can be achieved with time.

Since the aluminum is covered with a passive film of oxide in normal atmospheric condition, the frictional interaction between the aluminum pin and the oxide film is, in fact, the interaction between the oxide film on the pin surface and the substrate surface (oxide-oxide interaction). Hiratsuka et.al. [7] reported that, in the presence of oxygen, for metals with high standard heat of oxide formation, the coefficient of friction decreases. Since aluminum has high standard oxidation enthalpy (1676.8 KJmol^{-1} [7]), the coefficient of friction is expected to be less than that of pure aluminum. The initial coefficient of friction value for our experiment was observed to have a mean of 0.47 (Fig. 6).

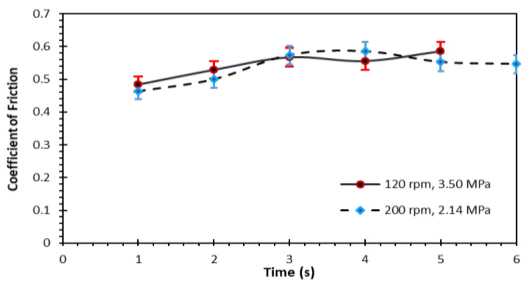

Fig. 5. Coefficient of friction values for annealed sample at 120 rpm/3.50 MPa and 200 rpm/2.14 MPa. Error bars at 5% error is also shown.

A qualitatively equal amount of wear was observed on the aluminum tip and the oxide film in this work. The shear strength of Al_2O_3 and Aluminum was comparable (921 MPa Al_2O_3 and 304 MPa for aluminum [7]) and the observation of the pin and oxide film wear was as expected.

Examination of the wear tracks showed that with increase in speed more wear happened on the oxide film. It could be because of the brittle nature of film and the wear is directly proportion to tangential velocity.

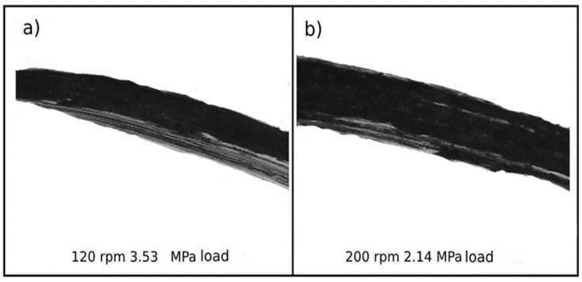

Fig. 6. Optical microscope photograph of wear track for annealed sample at 80x magnification: (a) 120 rpm/3.53 MPa; (b) 200 rpm/2.14 MPa.

Hiratsuka et al [7], conducted an experiment to understand the interaction of aluminum oxide with aluminum in vacuum. A good wear was observed on aluminum tip and literally no wear on aluminum oxide. However, the worn-out particles of aluminum formed a film on aluminum oxide surface which protected it from wear. A strong adhesive force exists between aluminum/aluminum interaction and its oxide interactions in atmospheric and vacuum conditions. However, such an experiment was not included in this study.

C. Aluminum Substrate Treated with Oxalic Acid

The substrate aluminum sheet was made to react with 0.16 molar aqueous solution of oxalic acid, heated and kept at a constant temperature of 80 ^{0}C for 1 hour. The pin on disk tribology test was conducted on the sample and the result is shown in Fig. 7.

It was observed that the oxalic acid treated sample had a considerable decrease in the friction coefficient when compared to thermally oxidized sample. As the time increased the coefficient of friction value started converging to the value obtained for interaction between pure aluminum tip and substrate.

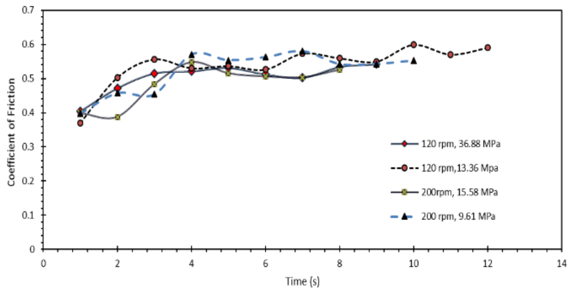

Fig. 7. Coefficient of friction values for chemically treated with oxalic acid/ aluminum interactions at different speeds and pressure

The reaction of oxalic acid with aluminum at room temperature, aluminum oxalate was formed as the product. However, our experiment is conducted at 80 ^{0}C. Young et.al [13] reported that the aluminum oxalate trihydrate was stable only up to a temperature 60 ^{0}C and it decomposed to different phases of aluminum oxide with temperature and cooling rate. The oxide film formed was amorphous and hydrous [14]. The XRD pattern of this film did not show any peaks other than for aluminum substrate which confirmed its amorphous nature.

The coefficient of friction value for the amorphous film was reduced to 0.39 in the beginning compared to annealed sample (0.47). The complete decomposition of oxalate to aluminum oxide was not achieved at this temperature [15]. Presence of hydroxide and moisture in the film might be the reason for the low friction coefficient in the beginning (Fig. 7). The wear track of the experiment is shown in Fig. 8.

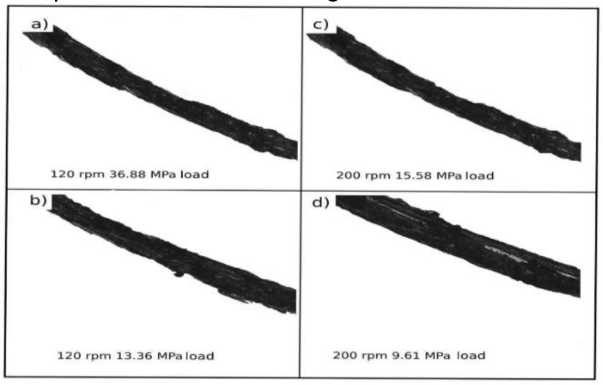

Fig. 8. Optical microscope photograph of wear track of chemically treated with oxalic acid /aluminum interaction at 80x magnification: a) 120 rpm/36.88 MPa; b) 120 rpm/13.36 MPa; c) 200 rpm/15.58 MPa; and d) 200 rpm/9.61 MPa.

As expected, the normal pressure on the film decreased with increase in speed. Also, the wear track for the last observation was not uniform as the other observation. The pin underwent considerable wear and its tip had wear tracks. This showed strong adhesive interaction between aluminum and its oxide.

D. Aluminum substrate treated with oxalic acid followed by annealing

The decomposition of aluminum oxalate with time and temperature had been studied in the past to understand the corrosion of aluminum by carbon dioxide [13]. The decomposition was a complex process and the phases of alumina obtained depended on the heating rate, final temperature and water content in the initial sample. Brown et.al. [16] discovered that aluminum oxalate decomposes to α-alumina at a temperature around 1000 ^{0}C whereas γ-$Al_2 0_3$ phase is produced at temperature above 350 ^{0}C. The phase transition usually follows $Al_2 0_3$ (amorphous) →γ → δ → Ɵ → α[14].

Since the sample was annealed at a constant temperature of 400 ^{0}C, γ - $Al_2 0_3$, was the dominant oxide phase observed in the XRD pattern. Also, a peak corresponding to gibbsite or aluminum hydroxide was also seen. Sato et.al [14] during thermogravimetric analysis of aluminum salts observed a weight loss of 62% corresponding to formation of alumina at 350 ^{0}C. It is confirmed that conversion into alumina was not quite complete even at 600 ^{0}C [15]. The presence of hydroxide and γ - $Al_2 0_3$ in the XRD (Fig. 11) correlates with the earlier works [14-16].

As mentioned above, the XRD pattern of annealed sample showed peaks; Gibbsite (220) at 41.8 ^{0}, and γ-Al_2O_3(321) at 44.3 ^{0} [17–21]. No peak other than that for aluminum substrate was seen in the XRD pattern of unannealed sample. The annealing recrystallized the sample and γ-Al_2O_3 is expected to be present at this temperature along with traces of hydroxides.

The results obtained for chemically oxidized and annealed sample is shown in Fig. 9. The coefficient of friction values were found to be more compared to other cases. From the XRD pattern it was observed that annealing recrystallized the film and made it hard. The chemically treated and annealed sample had a mean coefficient of friction value of 0.61 in the beginning.

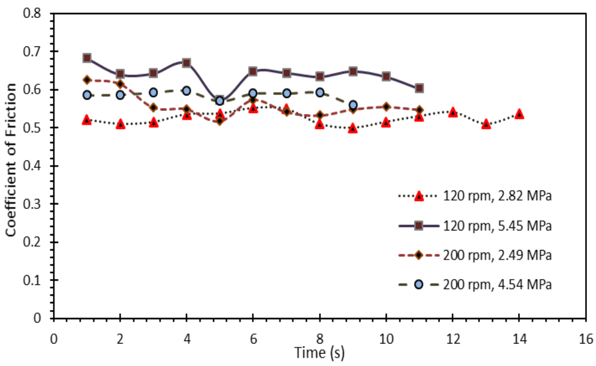

Fig. 9. Coefficient of friction values for chemically treated with oxalic acid and annealed/ aluminum interactions at different speeds and pressure.

Wear tracks for annealed and chemically treated sample is also shown in Fig. 10. The width of the wear tracks at 120 rpm were less than for 200 rpm. As explained earlier the wear was dependent on the sliding velocity and increased with speed.

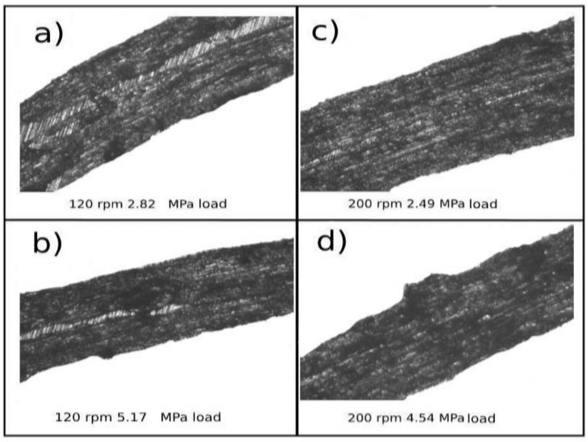

Fig. 10. Optical microscope photograph of wear track of chemically treated with oxalic acid /aluminum interaction at 80x magnification: (a) 120 rpm/2.82 MPa; (b) 120 rpm/ 5.17 MPa; (c) 200 rpm/2.49 MPa; and (d) 200 rpm/4.54 MPa.

In all the above studies it was observed that aluminum oxide film is worn off very quickly in less than 10 cycles. This give confirmation on the brittle nature of the film and would not act as a protective coating in tribological applications. But oxide films could protect the aluminum metal in corrosive environment. Also, as the speed was increased the wear rate also increased.

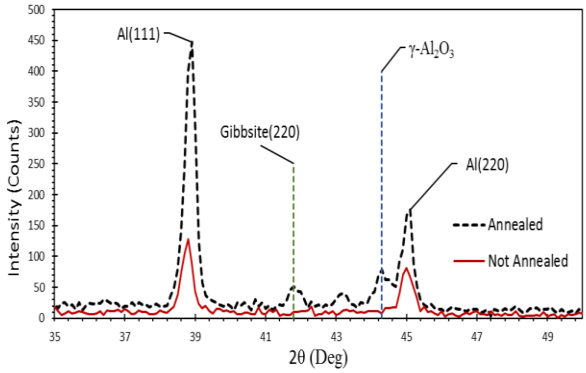

Fig. 11. X-ray diffraction pattern of annealed and unannealed sample of aluminum oxide film prepared by chemical oxidation with oxalic acid.

IV. CONCLUSION

A steady coefficient of friction value of between 0.6 and 0.5 has been observed for pure aluminum-aluminum with good surface interaction. The thermal oxidation resulted in oxide film growth which reduced the friction coefficient. Both the results of the experiment were acceptable and correlates with the past works in this field. Anodic oxidation of aluminum using oxalic acid solution as electrolyte is extensively investigated due to the porous nature of the film grown. The oxidation of aluminum with 0.166 molar solution of oxalic acid showed more reduction in friction coefficient with a mean of 0.39 in the beginning. The XRD confirmed the amorphous nature of as deposited oxide film with no dominant peaks corresponding to any aluminum oxide phase. The high affinity of oxalic acid to water adsorbs moisture on to the surface and which in turn reduced the friction coefficient. When the chemically treated sample is annealed the XRD peaks showed a crystalline γ-Al_2O_3 phase. Annealing recrystallized the sample and crystalline phases of the oxide and hydroxide was observed in the XRD. The coefficient of friction value was the highest for the chemically treated and annealed sample.

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