Corrosion Behavior and Hardness of Al–*M* (*M*: Mo, Si, Ti, Cr) Alloys

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Abstract The corrosion behavior of Al–5 at.% Cr, Al–5 at.% Si, Al–5 at.% Mo and Al–5 at.% Ti produced via casting and Al–5 at.% Cr produced by high-energy ball milling and subsequent consolidation by cold pressing was studied using potentiodynamic polarization and surface analysis following constant immersion tests. Alloys were characterized using a scanning electron microscope coupled with the energy-dispersive X-ray spectroscopy and X-ray diffraction analysis. Hardness, a representative of the strength, was also measured. The alloys produced by casting contained coarse intermetallics and therefore exhibited poor corrosion resistance. Al–5 at.% Cr alloy produced by high-energy ball milling exhibited a significantly improved corrosion resistance and hardness, which was attributed to the grain refinement to nanoscale and extended solid solubility of Cr in Al. The study indicated that the high-energy ball milling was capable of producing Al alloys with improved corrosion behavior and hardness.

KEY WORDS: Corrosion; Mechanical alloying; Casting; Aluminum alloys

1 Introduction

Pure aluminum is a very soft metal, and therefore it is alloyed with other elements to increase the strength [1, 2]. However, solubility of most of the elements in Al is limited and alloying elements as well as impurities have been reported to form intermetallics during processing and service conditions [1–3]. The electrochemical characteristics of the intermetallics are significantly different than those of the Al matrix, which renders the alloys prone to pitting corrosion [4–7]. The strength of age hardenable Al alloys relies on the precipitation strengthening, and therefore any attempt made to increase the strength often results in

increased corrosion. Developing high-strength and corrosion-resistant Al alloys is challenging but of great importance.

The corrosion behavior of Al alloys depends upon the characteristics of the intermetallics and matrix, and therefore understanding the influence of the chemical composition, morphology, and number of the intermetallics on corrosion behavior is of paramount interest. It has been shown recently that development of Al alloys with improved properties is possible by controlling the characteristics of the intermetallics and matrix via suitable alloying additions and processing techniques [8]. Some less common alloying elements including the rare earth and transition metals (such as Sc, Er, Zr, Ce, Mn, Nd, Cr, and Ag) are reported to enhance corrosion resistance by modifying the characteristics of the intermetallics [9–14]. For instance, addition of 0.4 wt% Ag to an Al–4Mg–1Cu–0.5Si alloy was reported to improve corrosion resistance by changing the morphology and composition of the precipitates [12]. Addition of Sr (as less as 0.08 wt%) to Al–Mg alloys has been reported to improve sensitization resistance

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by suppressing Mg_2Al_3 formation. Similarly, 0.1 wt% Nd has been reported to improve sensitization resistance of Al–Mg alloys by disrupting the interconnected network of Mg_2Al_3 phase on the grain boundaries during service conditions [13, 15]. Additions of Cr, Zr, and Nb to AA7075 were reported to increase the corrosion performance by decreasing the recrystallization tendency [9].

Unconventional alloy production techniques, i.e., sputtering and high-energy ball milling, have been reported to impart remarkable improvement in the pitting corrosion resistance. For example, Al–Cr, Al–Mn, Al–Mo, Al–Ta, Al–W, Al–Ti thin films produced by the sputtering processes have been reported to evince a significantly improved pitting potential [16–19]. This improvement was attributed to the extended solid solubility of alloying elements caused by the sputtering process. Recently, Frankel et al. [20] reported that improvement in pitting potential of the sputtered thin films of pure Al was also influenced by the incorporation of oxygen in the Al matrix. High-energy ball milling has also been shown to impart significant improvement in corrosion resistance of Al alloys. For example, Gupta et al. [21, 22] produced Al–Cr alloys with a wide range of Cr content and reported significant improvement in corrosion resistance and strength, which was attributed to the increased solid solubility of Cr and grain refinement to nanoscale. Work of Gupta et al. was supported by Seikh et al. [23] who produced Al–Cr alloys and reported significant improvement in the corrosion resistance in spite of presence of relatively coarser intermetallics. The high-energy ball-milled alloys have been reported to contain intermetallics of various sizes and compositions [21, 22, 24, 25], and therefore there is merit in studying the corrosion behavior of high-energy ball-milled alloys. Moreover, the unconventional alloying elements (i.e., Cr, Mo, Ti etc.) have been reported to induce significantly improved corrosion resistance when produced by sputtering or high-energy ball milling. The corrosion behavior of such Al alloys produced by casting is not reported in the literature. In the present study, Al–Cr, Al–Mo, Al–Ti, and Al–Si alloys were produced by casting to study their corrosion behavior and compare it with an Al–Cr alloy produced by high-energy ball milling.

2 Experimental

2.1 Alloy Synthesis by Casting

The raw materials used to produce cast alloys were aluminum pellets (purity 99.99% and size 1/4''–1/2''), aluminum powder, and alloying elements in the form of the powder. Prior to melting, the powder of aluminum and alloying elements were mixed and consolidated into pellets

of 12 mm diameter under uniaxial pressure of 200 MPa. The consolidated pellets contained 50 wt% alloying element. The casting was performed in graphite crucibles. Pure aluminum pellets were initially melted in the furnace at 700 °C. The temperature of the furnace was increased to the liquidus temperature of the desired alloy composition subsequently. The melting temperatures for Al–5 at.% Cr, Al–5 at.% Si, Al–5 at.% Mo, and Al–5 at.% Ti were 920, 700, 1240, and 1170 °C, respectively. Consolidated pellets containing 50 wt% alloying element were added to the melt at a regular interval of 1 h to achieve the desired composition. The liquid metal was stirred after addition of pellets. Once the desired composition was attained by the addition of the pellets, the melt was kept at the melting temperature for 1 h and was poured into a preheated steel mold. The alloys were homogenized at 450 °C for 25 h. The alloys produced by casting and subsequent homogenization are termed as “cast alloys” in this study. The compositions of the alloys after production were not determined, and nominal compositions of the alloys are reported herein.

2.2 Alloy Synthesis by High-Energy Ball Milling

An Al–5 at.% Cr alloy was synthesized via high-energy ball milling to compare the corrosion behavior and hardness with the cast alloys. Cr powder (purity 99.8%, size –100 mesh) and aluminum powder (purity 99.7%, size –50/+100 mesh) were loaded in the hardened steel jars with hardened steel balls (10 mm diameter) in a glove box containing high-purity Ar (oxygen content <25 ppm). Stearic acid (1.5 wt%) was used as process controlling agent (PCA). Steel jars were sealed in the glove box (high-purity Ar atmosphere) so that the Ar atmosphere can be maintained during the high-energy ball milling. High-energy ball milling was performed in a planetary mill at a speed 280 r/min for 100 h. The high-energy ball mill was interrupted for 30 min after every 1 h of ball milling. The high-energy ball-milled powder was consolidated using an autopellet press in a hardened steel die under a uniaxial pressure of 500 MPa for 20 min. The Al–5 at.% Cr alloy thus produced is termed as nanocrystalline (nc) Al–5 at.% Cr in this study.

2.3 Characterization by Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX)

The sample preparation for the characterization involved polishing up to 1 μm followed by ultrasonic cleaning in ethanol for 5 min. SEM was performed in a TescanLyra 3 FIB-FESEM in backscatter electron (BSE) mode at an accelerating voltage of 15 kV. Energy-dispersive X-ray

spectroscopy (EDXS) analysis was also performed to analyze the composition of the different phases present in the structure. A minimum of three point scans were performed to characterize the chemical composition of each phase.

2.4 Characterization by X-Ray Diffraction (XRD) Spectroscopy

The alloys for XRD were ground up to 600 grit SiC. XRD analysis was performed using a $\text{CuK}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$) to estimate the grain size and formation of intermetallics. The scanning speed was 1.0 deg./min with a step size of 0.1° . The grain size was calculated using the Scherrer's equation [26] after removing the instrumental broadening, which was determined from an annealed pure Al sample.

2.5 Corrosion Tests

Corrosion behavior of the produced alloys was studied using potentiodynamic polarization using a VMP-300 potentiostat. Sample preparation involved grinding up to 1200 grit SiC sandpaper followed by rinsing with copious amounts of water, ethanol, and drying. Corrosion tests were carried out in a conventional three-electrode electrochemical cell, using a graphite counter electrode and a saturated Ag/AgCl reference electrode. All tests were performed in 0.01 mol/L NaCl ($\text{pH} = 6.4$ and $\text{pH} = 3$) at room temperature using a scan rate of 1 mV/s . The pH of 3 was achieved by adding appropriate amount of sulfuric acid to 0.01 mol/L NaCl . The open circuit potential was monitored for 40 min, ensuring stabilization of the surface prior to potentiodynamic polarization tests. The change in open circuit potential with time was not significant after 15 min. Potential scans were performed in the cathodic direction, then left to stabilize the open circuit potential for another 40 min, and afterward polarized in the anodic direction until a current density of $100 \mu\text{A/cm}^2$. Experiments were repeated at least three times. The corrosion current density for the five alloys was determined using the Tafel extrapolation.

The corrosion behavior was also studied by immersion tests. The specimens were polished up to $1 \mu\text{m}$ followed by ultrasonic cleaning in ethanol for 5 min. The immersion tests were performed in 0.01 mol/L NaCl for 24 h, and the surface was analyzed by SEM subsequently.

2.6 Hardness Testing

Vickers hardness was measured using a Wilson Tukon 1202 Vicker hardness tester. Samples were ground until 1200 grit SiC sandpaper before testing. The applied load

was 25 g, and dwelling time of the indenter was 10 s. Hardness measurements were repeated 10 times.

3 Results

3.1 Characterization by SEM, EDXS, and XRD

SEM was used to characterize the morphology and composition of the intermetallic phases. Figure 1 shows the SEM images of cast alloys along with nanocrystalline Al–5 at.% Cr alloy. High-magnification SEM images are also presented in Figs. 2 and 3. Formation of coarse intermetallics was observed in all the cast alloys, which is expected due to the limited solubility of the alloying elements (Cr, Mo, Ti, Si) in Al [3, 27]. On the contrary, the intermetallics in nanocrystalline Al–5 at.% Cr alloy were significantly refined (Figs. 1e, 3). XRD scans for cast and high-energy ball-milled alloys are presented in Fig. 4, which indicated the formation of various intermetallics

XRD analysis (Fig. 4) indicated the formation of Al_7Cr intermetallics in cast Al–5 at.% Cr alloy, which were also revealed by SEM (Fig. 1a). Formation of Al_7Cr is also expected from the Al–Cr phase diagram [3]. The size of the smallest intermetallic was about $30 \mu\text{m}$. High-magnification SEM analysis also revealed the presence of oxygen inclusions in the matrix (Fig. 2a, top left corner). The chemical composition of the oxide inclusions was determined to be 17.92 at.% Cr, 2.59 at.% Al and 79.49 at.% O. Some of these intermetallic particles fell off from the surface during the grinding process. Furthermore, a Cr peak at $2\theta = 44.1$ is observed in the XRD pattern (Fig. 3), which is indicative of unalloyed Cr or Cr–Al solid solution.

Al–5 at.% Mo consisted of three phases: a bright phase, a gray phase, and a dark phase (Figs. 1b, 2b). EDXS point analysis indicated presence of significant amounts of Mo, 9.60 and 5.18 at.% in gray and bright phases, respectively, along with considerable amount of carbon. XRD analysis revealed presence of three phases: Mo_2C , Al_{12}Mo , and fcc Al. The formation of molybdenum carbide is thermodynamically feasible [28] and is expected due to the meting at significantly high temperature in graphite crucible.

Silicon is known to exhibit significant solubility in aluminum (maximum solid solubility of 2.6 at.%). Excess silicon (5 at.% in this study) tends to precipitate as secondary silicon at the eutectic temperature during solidification. Three main phases (bright, gray, and dark) were observed (Figs. 1c, 2c). The EDXS point analysis indicated a significant difference in the composition of the three phases. The bright phase contained 22.27 at.% Si and was believed to be primary silicon formed by the eutectic decomposition. The gray phase (containing 4.83 at.% Si)

Fig. 1 Backscatter electron images for **a** cast Al-5 at.% Cr, **b** cast Al-5 at.% Mo, **c** cast Al-5 at.% Si, **d** cast Al-5 at.% Ti, **e** nanocrystalline Al-5 at.% Cr alloys

Fig. 2 Backscatter electron images for **a** cast Al-5 at.% Cr, **b** cast Al-5 at.% Mo, **c** cast Al-5 at.% Si, **d** cast Al-5 at.% Ti, **e** nanocrystalline Al-5 at.% Cr alloys. Matrix (α) and secondary phases are marked

was expected to be silicon formed by the decomposition of the Al-Si solid solution during homogenization at 450 °C. The dark phase, matrix, consisted 0.66 at.% Si in solid solution. Thermodynamic calculations performed using

software PANDAT predicted only 0.26 at.% Si in the solid solution at the homogenization temperature [29], and discrepancy between these values could be due to the semi-quantitative nature of the EDXS analysis caused by large

Fig. 3 SEM image for nanocrystalline Al-5 at.% Cr. Matrix (α^*) and secondary phases are marked

Fig. 4 XRD patterns for cast Al-5 at.% Cr, cast Al-5 at.% Mo, cast Al-5 at.% Si, cast Al-5 at.% Ti and nanocrystalline (NC) Al-5 at.% Cr alloys

interaction volume or presence of silicon in a metastable state in solid solution.

Coarse intermetallics were observed in the cast Al-5 at.% Ti alloy (Figs. 1d, 2d). EDXS analysis indicated the presence of 0.7 at.% Ti in the matrix and 23.58 at.% Ti in the intermetallics (appearing bright), which is close to the theoretical composition of the intermetallic Al_3Ti . XRD analysis (Fig. 3) corroborated the presence of Al_3Ti . The Al-Ti phase diagram also suggests the presence of fcc α matrix and Al_3Ti intermetallic for Al-5 at.%Ti. PANDAT calculations indicated 0.095 at.%Ti in the matrix at homogenization temperature, which is significantly lower than that detected by EDXS.

Figures 1e and 3 show the microstructure of nanocrystalline Al-5 at.% Cr. The size of the intermetallics was

significantly refined. The biggest interparticle was about 3 μm , and fine particles ($<500\text{ nm}$) were uniformly distributed in the matrix. Significant porosity was also visible (Fig. 1e), which was attributed to the relatively low consolidation pressure and high strength of the high-energy ball-milled Al-5 at.% Cr alloy. EDXS analysis detected 4.28 at.% of chromium in the matrix phase, which is significantly higher than the Cr content expected from the phase diagram. The second phase particles had a composition similar to that of Al_7Cr (12.5 at.% Cr). XRD analysis corroborated the presence of Al_7Cr . In addition, a pure Cr peak at a 2-theta value of 44.1 was also distinguished [30]. Significant peak broadening in nanocrystalline Al-5 at.% Cr alloy was observed (Fig. 4) which indicated a nanocrystalline structure. The grain size for nanocrystalline Al-5 at.% Cr was determined to be 31 nm.

3.2 Potentiodynamic Polarization

Potentiodynamic polarization curves for the four cast alloys and nanocrystalline Al-5 at.% Cr in 0.01 mol/L NaCl (pH = 6.4) are presented in Fig. 5a, which clearly show the superior corrosion behavior Al-5 at.% Cr alloy produced by high-energy ball milling and subsequent compaction. Cathodic current density for the cast alloy was significantly higher, which is expected due to the presence of coarse cathodic particles capable of escalating the cathodic reaction rate. Anodic current density for nanocrystalline alloy was significantly lower than that for the cast alloys, which indicates that the extended solid solubility and grain refinement induced by high-energy ball milling were capable of inhibiting the anodic reaction. The cast alloys did not show any passive region, indicating onset of the pitting corrosion at or below the corrosion potential. On the contrary, nanocrystalline alloy exhibited clear passive region (difference between corrosion potential and pitting potential in Fig. 5a) indicating excellent passivation behavior and pitting corrosion resistance. It is noteworthy that the nanocrystalline Al-5 at.% Cr was not fully consolidated, yet the corrosion behavior was excellent. Improvement in the consolidation process is expected to augment the corrosion behavior.

Potentiodynamic polarization tests were also performed in 0.01 mol/L NaCl with a pH = 3, and results are presented in Fig. 5b. Similar to the results in pH = 6.4, the corrosion behavior of the nanocrystalline alloy was superior to cast alloys. A decrease in pH caused a significant decrease in the corrosion potential and an increase in current densities. Pitting potential for the nanocrystalline Al-5 at.% Cr was significantly higher than that of the cast alloys (Fig. 5b) at pH = 3.

The corrosion current densities of the five alloys, determined using Tafel extrapolation, are presented in

Fig. 5 a Potentiodynamic polarization curves for the cast alloys and nanocrystalline Al-5 at.% Cr in 0.01 mol/L NaCl (pH = 6.4), b potentiodynamic polarization curves for the cast alloys and nanocrystalline Al-5 at.% Cr in 0.01 mol/L NaCl (pH = 3)

Fig. 6 Corrosion current density for cast alloys and nanocrystalline Al-5 at.% Cr as determined from the potentiodynamic polarization tests

Fig. 6. The corrosion current density for the nanocrystalline Al-5 at.% Cr alloy was significantly lower than that for the cast alloys in both solutions. It is very interesting to compare the influence of various alloying elements on the cathodic and anodic current densities in four cast alloys. The cathodic current density was highest for Al-5 at.% Mo and lowest for Al-5 at.% Ti and Al-5 at.% Si, indicating that the deleterious influence of cathodic intermetallics in accelerating the localized corrosion was relatively moderate in Ti- and Si-containing alloys. Anodic and cathodic current densities for the nanocrystalline Al-5 at.% Cr alloy were significantly lower than those for the four cast alloys, which was attributed to the refined microstructure and

incorporation of Cr in the matrix due to the high-energy ball milling.

The corrosion behavior was further evaluated by the immersion of the test specimen in the 0.01 mol/L NaCl (pH = 6.4) for 24 h. Visual inspection of test specimen after 24-h immersion suggested significant corrosion in the cast alloys, whereas no corrosion was observed in the nanocrystalline Al-5 at.% Cr. The SEM images of the alloys after immersion tests are presented in Fig. 7. Significant corrosion of the matrix phase occurred in the cast alloys, whereas corrosion in the nanocrystalline Al-5 at.% Cr was least, which supplements the conclusions from the potentiodynamic polarization tests. Corrosion products in nanocrystalline Al-5 at.% Cr were observed only in isolated small regions and are shown in Fig. 7.

3.3 Hardness

The cast alloys consisted of two phases: matrix and intermetallics. The hardness of the both the phases was determined using the microhardness tester under an applied load of 10 g. The hardness measurements were performed for at least 10 times. Average Vickers hardness number (H_m) for the matrix of Al-5 at.% Mo, Al-5 at.% Ti, and Al-5 at.% Cr was 21 (± 1.9), 26.5 (± 3.2), and 21 (± 1.2), respectively. The hardness of the secondary phase particles (H_{sp}) was significantly higher and was measured to be 204.1 (± 27.1), 415.2 (± 58.2), and 298.2 (± 26.1) for the Al-5 at.% Mo, Al-5 at.% Ti, and Al-5 at.% Cr, respectively. The uniformly distributed secondary phase particles in Al-5 at.% Si and the nanocrystalline Al-5 at.% Cr were too fine to perform microhardness measurements on them. Average hardness of the matrix was measured to be 32.6

Fig. 7 Secondary electron images for **a** cast Al-5 at.% Cr (low magnification), **b** cast Al-5 at.% Cr (high magnification), **c** cast Al-5 at.% Mo (low magnification), **d** cast Al-5 at.% Mo (high magnification), **e** cast Al-5 at.% Si (low magnification), **f** cast Al-5 at.% Si (high magnification), **g** cast Al-5 at.% Ti (low magnification), **h** cast Al-5 at.% Ti (high magnification), **i** nanocrystalline Al-5 at.% Cr (low magnification), **j** nanocrystalline Al-5 at.% Cr (high magnification) alloys

(± 1.8) for cast Al–5 at.% Si and 198.8 (± 18.6) for nanocrystalline Al–5 at.% Cr.

For cast Al–5 at.% Cr, Al–5 at.% Mo, and Al–5 at.% Ti, the overall hardness was estimated using a rule of mixtures [31] according to the following equation:

$$HV_{\text{estimated}} = f_m H_m + f_{sp} H_{sp},$$

where f_m and f_{sp} are the area fractions of the matrix and secondary particles, respectively, and H_m and H_{sp} are the hardness of the matrix and the secondary phase particles, respectively. Area fractions (f_m and f_{sp}) were determined using the image analyzer software Image J [32]. The area fraction of the secondary phase particles for Al–5 at.% Mo, Al–5 at.% Ti, and Al–5 at.% Cr was determined to be 0.37, 0.19, and 0.047, respectively.

The estimated Vickers hardness of the cast alloys and measured hardness of the nanocrystalline Al–5 at.% Cr alloy are presented in Fig. 8. Hardness of annealed pure Al is also included for the comparison. The hardness of the nanocrystalline alloy was significantly higher than that of the cast alloys. The high hardness of nanocrystalline Al–5 at.% Cr alloy was expected due to the extended solid solubility, grain refinement, and uniformly distributed of fine intermetallic particles. The estimated hardness of the cast alloys was significantly higher than the pure Al, which was due to the presence of a significantly large fraction of intermetallics. It is noteworthy that the hardness of matrix was slightly higher than that of pure Al, which was attributed to the solid solution strengthening. The hardness of the matrix of cast Al–5 at.% Si was the highest followed by Al–5 at.% Ti, Al–5 at.% Cr, and Al–5 at.% Mo. The increase in hardness of the matrix is in the order of the maximum solubility of the alloying elements.

Fig. 8 Vickers hardness measured for nanocrystalline Al–5 at.% Cr and pure Al, and estimated from rule of mixture for the cast alloys

4 Discussion

The role of grain size, chemical composition of the matrix, and size and composition of the secondary phase particles has been discussed previously [33–38]. A decrease in size and area fraction of the cathodic particles is reported to cause a significant decrease in cathodic current density, pruning the deleterious influence of cathodic particles [6, 21, 36]. In the present work, nanocrystalline Al–5 at.% Cr showed significantly higher corrosion resistance and hardness than other cast alloys containing similar amount of alloying additions. Improved corrosion resistance of nanocrystalline Al–5 at.% Cr alloy is attributed to the refined microstructure and extended solid solubility caused by the high-energy ball milling process. Nanocrystalline Al–5 at.% Cr alloy contained significantly refined intermetallics, abating their capacity to sustain the cathodic currents. Additionally, Cr present in the solid solution is expected to increase the passivation behavior causing a significant diminution in anodic current density and pitting corrosion.

Improving the corrosion behavior and hardness concurrently is of great technological importance and explored recently [8, 12, 21, 22, 37, 39, 40]. The corrosion resistance and the hardness of the nanocrystalline Al–5 at.% Cr were superior. For comparison, the hardness of the alloys reported herein is plotted as a function of the current density (determined from Fig. 5a) in Fig. 9. AA-7075-T651 [41], representative of a high-strength Al alloy, is also included for comparison. Figure 9 clearly shows that the nanocrystalline alloys possessed superior corrosion resistance and hardness. High-energy ball milling was

Fig. 9 Vickers hardness number vs corrosion current density of cast alloys, nanocrystalline Al–5 at.% Cr and AA7075-T651

capable of engendering simultaneous improvement in corrosion and mechanical properties.

5 Conclusions

The four cast alloys (Al–5 at.% Cr, Al–5 at.% Si, Al–5 at.% Mo and Al–5 at.% Ti), produced by casting and subsequent homogenization, contained coarse intermetallics. The cast alloys exhibited poor corrosion behavior as investigated by potentiodynamic polarization tests and constant immersion tests followed by surface analysis by SEM. Hardness and the corrosion behavior of the cast alloys were influenced by the alloying elements.

A nanocrystalline Al–5 at.% Cr alloy was also successfully produced by high-energy ball milling followed by cold compaction. The nanocrystalline alloy exhibited significantly refined microstructure with maximum size of the intermetallic particles <3 µm and grain size of the of 31 nm. The corrosion resistance and hardness of the nanocrystalline Al–5 at.% Cr alloy were significantly higher than those of cast alloys, which was attributed to the ability of high-energy ball milling to impart grain refinement to nanoscale, extended solid solubility, and refinement of the secondary phases. This study showed that high-energy ball milling is capable of producing Al alloys with significantly higher corrosion resistance and hardness.

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