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Review—Corrosion-Resistant Metastable Al Alloys: An Overview of Corrosion Mechanisms

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Commercial aluminum alloys exhibit localized corrosion when exposed to environments containing aggressive anions. Alloying of Al with specific elements (M: Cr, Mo, V, Nb, etc) using non-equilibrium processing techniques has been reported to result in significantly improved corrosion resistance due to the formation of a supersaturated solid solution and uniform distribution of M in the matrix. Several theories describing the corrosion behavior of Al–M alloys have been postulated. This paper presents an overview of the most common non-equilibrium alloying techniques implemented for the production of the metastable Al–M alloys and posited corrosion mechanisms for the improved corrosion resistance.

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The development of high strength, lightweight, and corrosionresistant materials is critical to meet the current demand for lightweight and durable components for engineering applications leading to increased fuel efficiency and decreased carbon emission. Aluminum (Al) alloys offer excellent strength-to-weight ratio and therefore used widely in automotive, aerospace, and marine applications. However, the use of Al-alloys is constrained in many applications due to their limited corrosion resistance and a deterioration of the corrosion performance with efforts to increase the strength.¹⁻³ If Al alloys with high corrosion resistance, comparable with that of stainless steel, could be prepared, they could be future lightweight and environmentally friendly alloys. For designing such alloys, corrosion of Al alloys and its relationship with the composition and microstructure at various length scales must be understood. Fundamentals of corrosion of Al and its alloys and role of processing, microstructure, and composition on Al alloys can be found in.

Aluminum is a reactive metal, albeit it possesses excellent corrosion resistance due to the presence of a thin (typically 2-5 nm) surface oxide film known as a passive film.^{7,8} This film is stable in an aqueous environment in the pH range of 4.0 to 8.5.9 The integrity of the passive film is compromised in the presence of aggressive anions such as halides, and acidic and alkaline pH conditions. Therefore, the corrosion resistance of Al and its alloys is inferior to several corrosion-resistant alloys like stainless steel, titanium, and superalloys. The corrosion resistance of Al decreases further when it is alloyed with other elements to increase the strength. The solubility of most elements in Al is small and added alloying elements and impurities like Fe and Si form secondary phases: known as constituent particles, dispersoids, and precipitates depending upon the size and thermal stability.¹⁰ Electrochemical characteristics of the secondary phases have been reported to be significantly different than the matrix, and therefore a micro galvanic cell is formed, and localized corrosion occurs.^{7,8} Characteristics of the secondary phases (including composition, morphology, distribution) and matrix (composition, grain size) play a vital role in determining the corrosion performance of Al alloys. Secondary phases and matrix can be manipulated to improve corrosion resistance. Moderating the cathodic or anodic activity of the secondary phase by modifying composition or size can be one of the strategies to improve corrosion resistance.^{4,11} For instance, improving the stability of Mg₂Al₃ phase in 5xxx Al alloys by microalloying with Zn or Cu has been reported to improve the corrosion resistance.¹² Similarly, microalloying of Cu in 7xxx alloys is known to improve the corrosion resistance by

increasing the stability of anodic $MgZn_2$ phases.^{12–14} However, the highest achievable corrosion resistance by modifying the characteristics of the secondary phases would not surpass that for pure Al.^{1,4–6}

Modifying the composition of the matrix by incorporating wellknown corrosion-resistant elements could be a potential strategy for improving the corrosion resistance of Al alloys.^{1,15–17} Explored compositional space for the Al alloys is minimal. Various combinations of Cu, Mg, Zn, Si, and Mn have been used as primary alloying elements.¹⁸ Known corrosion-resistant alloying elements like Cr, Mo, Ni, Nb, Ti etc have seldom been used as principal alloying elements in commercial Al alloys because the solubility of these alloying elements in Al is negligible and therefore added alloying elements form coarse intermetallics. However, if the solid solubility of the alloying elements could be improved, a high corrosion resistance would be achieved.^{1,15–17}

Aluminum alloys with high solid solubility of certain alloying elements (M: Cr, V, Nb, Ta, W, Ta, Ti, Mo, Ni, V, etc) have been produced using non-equilibrium processing techniques and will be reviewed herein. The solubility of the alloying elements M was several orders of magnitude higher than that predicted by the phase diagram, and therefore the Al-M alloys remain in a metastable state. The Al-M alloys have demonstrated high corrosion resistance in various electrolytes. The pitting potential of the Al-M alloys, containing high solid solubility of M, in NaCl solution was reported to be even higher than that for corrosion-resistant stainless steel such as 304 L. Various mechanisms for such improved corrosion resistance have been proposed in the literature. Role of the alloying elements on the stability, breakdown and repairing of the passive film has been considered by a number of investigators. This paper presents a comprehensive review of the proposed corrosion mechanisms for the improved corrosion resistance of Al-M alloys. This discussion is useful not only in understanding the corrosion behavior of Al-M alloys but also help in developing new Al alloys by leveraging modern manufacturing technologies able to engineer the desired microstructure.

Manufacturing Technologies For the Production of Metastable Al–M Alloys Exhibiting High Solubility of the Alloying Element (M)

The alloys produced by non-equilibrium alloying techniques, able to impart high solid solubility of the alloying elements, have been reported to exhibit nanocrystalline or amorphous structures and supersaturation of the alloying elements that are considered to have negligible solubility in Al. For example, the room temperature solubility of Ti in Al is negligible, and therefore Al–Ti alloys produced by casting consist of coarse intermetallics. On the contrary high-energy ball milled Al–Ti alloys exhibited high solid solubility



Figure 1. Backscattered electron images for Al-5at%Ti produced by (a) casting, and (b) high-energy ball milling and subsequent cold compaction.¹⁹

and absence of coarse intermetallics.¹⁹ Figure 1 clearly shows the difference between the microstructure of the Al-5at%5Ti alloy produced by casting and high-energy ball milling followed by cold compaction. X-ray diffraction analysis further showed that high-energy ball milling imparted high solid solubility of the Ti in Al.¹⁹ The high solid solubility of the alloying elements, grain refinement, and homogenous microstructure are reported to enhance corrosion resistance. The following sections present an overview of selected non-equilibrium alloying techniques that have been used to produce Al alloys exhibiting properties far superior to what is commonly found in conventional alloys.

Ion implantation (II) and ion beam mixing (IBM) for enriching the surface of Al with selected solute elements (M).—Ion implantation (II), a routinely used technique in the semiconductor industries, allows the bombardment of accelerated ions into the surface of the alloy,²⁰ forming an altered surface layer up to 100 nm deep with significantly different physical and chemical properties than the bulk alloy. II has been performed on the Al alloys to achieve a supersaturated solid solution of unconventional alloying elements, such as transition metals.^{15,21–26} The corrosion resistance of the Al alloys after ion implantation of Mo,^{21–25,27} Ar,²⁸ Cr,²⁹ Ta,^{30–32} Ni,²⁷ Pb, Si,²⁴ Nb,²⁴ Zr,²⁴ Cr,²⁶ Ti²⁶ and V²⁶ has been studied and a significant improvement in the corrosion resistance have been observed. Table I shows a compendium of ion-implanted Al alloys. The solute concentration was depth-dependent across the enriched surface. which was estimated using diverse analytical techniques. To provide a fair comparison, ion implantation settings of accelerating voltage and dosage concentration is presented instead. The choice of the elements for the ion implantation to improve the corrosion resistance was based on several criteria. Natishan et al.²⁴ envisioned that an element capable of producing an oxide with a lower pH of zero charge than Al₂O₃, should diminish the electrostatic adsorption of Cl⁻ and therefore retard the passive film breakdown. Ability to increase passive film thickness²¹ or enrichment of the implanted ions in the passive film^{22,26} were some of the other criterion for the choice of the elements.

The ion implantation machine used in initial investigations was complex with exorbitant energy requirements.²¹ Therefore, a simpler

version of ion implantation, known as Ion beam mixing (IBM), was developed and implemented for Al alloys.^{22,25} Attempts to modify surfaces by implantation of Mo^{22,25} and Cr²⁵ using IBM at low accelerating voltages did not result in any significant improvement in corrosion resistance. Interestingly, Zeller et al.²² compared the micrographs of Al and Mo implanted Al after 24 h of immersion in chloride solution and concluded that IBM resulted in higher pitting corrosion. Auger data suggested that Mo rich zones formed, which were cathodic to the Al matrix and caused galvanic corrosion. Natishan,²⁵ using XPS analysis, reported that the majority of the implanted alloying element was deposited as a pure metal on top of the original air-formed oxide film that was present in the Al target and the IBM was not further explored for modifying the surface for improved corrosion resistance.

Ion implantation was the first reported technique for causing supersaturation of the alloying elements in Al and improving corrosion resistance substantially. Investigators realized the potential of improving corrosion resistance by high solid solubility of unconventional alloying elements in Al. However, II or IBM could not be used in engineering applications because of several challenges: inhomogeneity of implanted zones causing galvanic corrosion, coating defects and their possible interaction with the underlying substrate, complications in the selection of adequate alloying elements, high cost of the technique, and upscaling production. Nonetheless, a new concept of improving corrosion resistance was established for future research.

Magnetron sputtering for the production of the thin films.— Magnetron sputtering (MS) is a technique that uses a magnetic field configured parallel to a target to where secondary electron motion is constrained. The magnets are arranged in such a way that all electron-atom collisions are condensed, forming a dense plasma at the surface of the target region.³³ Radiofrequency magnetron sputtering (RF-MS), typically using a frequency of 13.56 MHz, can produce high-quality films³³; however, deposition rates are lower compared to the MS modalities and the hardware set up required is complex imposing challenges in scaling up for commercial applications.³³ Nevertheless, RF-MS has been used to produce non-equilibrium Al alloys by directly depositing Al and alloying

Table I. Pitting potential of ion-implanted aluminum. The tests were performed in various NaCl concentrations in near-neutral solution.

Implanted element	Accelerating voltage (keV)	Dosage (ions cm ⁻²)	Electrolyte	Pitting potential (mV_{SCE})	References
Мо	20	10 ¹⁵	$0.01 \text{ M Na}_2 \text{SO}_4 + 1000 \text{ ppm Cl}^-$	-200	21
Si	65	$2.9 imes 10^{16}$	0.1 M NaCl	-340	24
Nb	95	$2.8 imes 10^{16}$	0.1 M NaCl	-585	24
Zr	25	10^{16}	0.1 M NaCl	-410	24
Cr	25	1.8×10^{16}	0.1 M NaCl	-565	24
Ν	30	10^{18}	3.5 wt% NaCl	-660	26
Ti	30	5×10^{17}	3.5 wt% NaCl	-580	26
V	30	10 ¹⁷	3.5 wt% NaCl	-605	26

Solute element	Solute concentration (at%)	Electrolyte	Pitting potential (mV_{SCE})	References
Nb	26.6	0.1 M NaCl pH 10	616.1	37
Та	25	0.1 M NaCl pH 10	461.3	37
Ti	25.4	0.1 M NaCl pH 10	151.6	37
V	9.7	0.1 M NaCl	61.5	17
Mn	15.7	0.1 M NaCl	-144.9	17
Мо	8	0.1 M KCl pH 7	66.5	38
Cr	4	0.1 M KCl pH 7	-96.5	38
Та	8	0.1 M KCl pH 7	-44.0	38
W	9	0.1 M KCl pH 7	1945.3	39

Table II. Pitting potential of Sputter-deposited alloys as determined in wide range of electrolytes using potentiodynamic polarization tests. The alloy thin films were produced by RF Magnetron sputtering.

element into a silicon target, allowing the alloying element to be retained in solid solution despite the equilibrium solubility being orders of magnitude smaller.³⁴

Considering the success of Mo implanted Al in increasing corrosion resistance,²¹ sputtered deposited Al–Mo alloys were developed alongside many other alloying elements.^{17,35–40} Table II shows selected sputter-deposited Al alloys and their pitting potential in various electrolytes. In particular, Al–W alloys exhibited an overwhelming improvement in pitting resistance with moderate W additions, as shown by the pitting potential through cyclic potentio-dynamic polarization. It should be noted that pitting potential was significantly higher than that for any commercial Al alloy. Sputtered deposited Al alloys by RF-MS had much better quality and control in their composition and microstructure; they did not suffer many of the shortcomings of ion-implanted alloys such as the formation of a top layer of pure alloying element. The ability to achieve complete solid solubility despite high solute concentrations imparted interesting and unique properties, such as improvement in the pitting resistance with an increasing solute concentration in Al–Mo alloys.⁴¹

The sputter-deposited alloys were either amorphous or crystalline with fine grain size.^{17,39,40} The grain size was reported to decrease with increasing solute content.^{17,39,41} It was later reported that both cooling rate during the sputtering process and solute concentration played an important role in the resulting structure of the alloys.⁴⁰ Solute elements were incorporated in solid solution as observed from a change in the lattice parameter by X-ray diffraction analysis.^{39,41}

In-depth studies on the chemistry of the passive oxide film provided mechanistic insight of the process controlling passivity in these alloys.^{38–40,42} XPS studies performed on Al–Mo alloys in chloride-containing near-neutral environment showed that the Mo content in the passive film was well below to what it was in the bulk alloy.⁴³ Similarly, only trace amounts of oxidized solute were found on Al–W³⁹ and Al–Cr⁴³ under the same conditions. Table III shows the surface chemistry of some sputter-deposited alloys after exposure to various environments. Except for Al–Zr and Al–Ta, preferential oxidation of Al occurred in near-neutral environments, and the passive layer was chemically similar to that for pure Al. Mechanisms proposed for high-corrosion resistance of these films by incorporation of only trace amounts of the solute element in the passive oxide film include structural stabilization,⁴² solute vacancy interaction model (SVIM)⁴⁴ and Solute-rich interface model (SRIM)^{40,45} which are discussed in detail in later sections.

Electrodeposition for the production of Al-M coatings.—The ionic liquids present an important technological advancement that enables the electrodeposition of the elements otherwise not possible in aqueous electrolytes.⁴⁷ Electro-deposition of Al in aqueous solutions is challenging due to the occurrence of hydrogen evolution reaction. Lewis Acidic Haloaluminate Room Temperature Ionic Liquids (RTILs) such as AlCl₃-1-ethyl-3-methylimidazolium chloride are capable of producing glassy Al-based alloys with quality and properties comparable to those produced by RF-magnetron sputtering.⁴⁷ This includes non-equilibrium Al-based

alloys such as Al–V,⁴⁸ Al–Mo,⁴⁹ Al–Zr,⁵⁰ Al–Mn,⁵¹ Al–Ti,⁵² Al–Wi⁵³ and Al–Nb.⁵⁴ The microstructure of the electrodeposited alloys consisted of complete supersaturation and structure varying from amorphous structures crystalline structure of grain size from nano to micron meter range. Variables such as the solute element, electrodeposition parameters and electrodeposition additives have been reported to influence the structure and composition of the electrodeposited alloys.⁵⁴

The pitting potential of some of these alloys, as measured by cyclic potentiodynamic polarization, is presented in Table IV. The corrosion resistance of electrodeposited alloys is comparable to their sputter-deposited counterparts, as presented in Table II. The high corrosion resistance of the Al allovs processed by sputtering has relied heavily on large quantities of elements like Cr, Mo, W, and Ni in solid solution. It is interesting to note the high pitting potential of the electrodeposited Al-Mn⁵¹ alloy. Mn is not considered passivating elements and not reported to improve the passivation in Al, Fe, or Ni-based alloys. However, Mn has a lower hydrolysis constant than Al. and this could decrease the rate of acidification and the formation of a critical pit environment that impeded the pit growth.¹ The pitting potential in both sputter-deposited and electro-deposited Al-Mn alloys was very close to the repassivation potential, which indicated higher passivation tendency and therefore increased pitting potential.

High-energy ball milling for the production of bulk Al–M alloys from powder metallurgical route.—High-energy ball milling (HEBM), also known as mechanical alloying, was originally invented to produce dispersed strengthened Ni superalloys.⁵⁵ The technique was later extended to many types of materials^{56–58} Al was of particular interest, considering that each particle of the initial powder would be naturally enveloped by an oxide film.⁵⁷ This oxide would then act as dispersed, strengthening particles after extensive mixing during milling.⁵⁷ The intricacies of the HEBM, as well as the microstructure and properties of alloys produced by this method have been overviewed thoroughly elsewhere.^{1,58}

High-energy ball milled Al alloys have mostly been produced with the purpose of increasing mechanical properties. Studying the corrosion resistance of Al-based alloys as produced by high energy ball milling has only attracted attention recently.^{1,3,59} In earlier studies, high-energy ball milled Al–Mg based alloys were produced, which did not show a significant difference in corrosion resistance.

Recently, Gupta et al. exploited the ability of HEBM in causing extended solid solubility in producing corrosion-resistant alloys with high strength.^{3,58,59} Their work proved that the combination of the high-energy ball mill technology with a suitable alloy composition could increase corrosion resistance and strength simultaneously. Despite the technique's shortcoming, the corrosion resistance of high-energy ball milled Al–Cr alloys was comparable to those produced by sputtering. This meant that the resulting microstructure was sufficiently influenced by the nanostructure and supersaturation to achieve significantly high corrosion resistance, and the refinement and distribution of secondary phases was adequate to avoid any

Alloy	Oxidizedsolute species	Oxidized solute/Oxidized Al at the surface	Metallic solute/Metallic Al substrate	Environment	Treatment	References
Al-7Mo	Mo^{4+}	7.53×10^{-03}	$7.53 imes 10^{-02}$	Air	Air-formed oxide film	41
Al-7Mo	Mo ⁴⁺	$1.10 imes 10^{-02}$	7.53×10^{-02}	Deaerated 0.1 N KCl pH 8	OCP stabilized	41
Al-7Mo	Mo^{5+} and Mo^{6+}	1.9×10^{-02}	7.53×10^{-02}	Deaerated 0.1 N KCl pH 8	Polarized to breakdown potential	41
Al-16Mo	Mo^{4+}	$7.07 imes 10^{-03}$	1.90×10^{-01}	Deaerated 0.1 N KCl pH 8	Polarized to -600 mV SCE	43
Al-16Mo	Mo ⁶⁺	$8.75 imes 10^{-03}$	1.90×10^{-01}	Deaerated 0.1 N KCl pH 8	Polarized to -600 mV SCE	43
Al-15Cr	Cr ³⁺	$8.42 imes 10^{-03}$	1.76×10^{-01}	Deaerated 0.1 N KCl pH 8	Polarized to -600 mV SCE	43
Al-8Ta	Ta ⁵⁺	$1.08 imes 10^{-01}$	8.70×10^{-02}	Deaerated 0.1 N KCl pH 8	Stabilized OCP	38
Al-8Ta	Ta ⁵⁺	5.26×10^{-01}	$8.70 imes 10^{-02}$	Deaerated 0.1 N KCl pH 8	Polarized to 800 mV SCE	38
Al-4Zr	Zr^{4+}	1.36×10^{-01}	4.17×10^{-02}	Deaerated 0.1 N KCl pH 8	Stabilized OCP	38
Al-4Zr	Zr^{4+}	$4.70 imes 10^{-01}$	4.17×10^{-02}	Deaerated 0.1 N KCl pH 8	Polarized to 800 mV SCE	38
Al-6W	W^{4+}	$3.05 imes 10^{-03}$	6.38×10^{-02}	Aerated 0.1 N KCl pH 7	Stabilized OCP	39
Al-6W	W^{4+}	4.12×10^{-03}	6.38×10^{-02}	Aerated 0.1 N KCl pH 7	Polarized to 1100 mV SCE	39
Al-6W	W^{6+}	2.31×10^{-03}	6.38×10^{-02}	Aerated 0.1 N KCl pH 7	Stabilized OCP	39
Al-6W	W^{6+}	$8.66 imes 10^{-03}$	6.38×10^{-02}	Aerated 0.1 N KCl pH 7	Polarized to 1100 mV SCE	39
Al-15W	W^{6+}	$2.27 imes 10^{-04}$	1.76×10^{-01}	Deaerated 1.0 M HCl pH 0	Stabilized OCP	46
Al-15W	W^{6+}	3.04×10^{-00}	1.76×10^{-01}	Deaerated 1.0 M HCl pH 0	Polarized to -200 mV SCE	46
Al-15W	W^{4+}	$5.67 imes 10^{-05}$	1.76×10^{-01}	Deaerated 1.0 M HCl pH 0	Stabilized OCP	46
Al-15W	W^{4+}	$9.60 imes 10^{-01}$	1.76×10^{-01}	Deaerated 1.0 M HCl pH 0	Polarized to -200 mV SCE	46
Al-3.6 W	Total W	$5.69 imes 10^{-01}$	3.85×10^{-02}	Aerated 0.1 M KCl pH3	Stabilized OCP	40
Al-3.6 W	Total W	9.19×10^{-01}	3.85×10^{-02}	Aerated 0.1 M KCl pH3	Polarized anodically 750 mV	40

Table III. Surface chemistry of Sputter-deposited alloys. The alloys were produced by the RF Magnetron sputtering and surface film was characterized using XPS after corrosion tests which is described in column treatment.

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Table IV. Pitting	potential of e	electro-deposited n	on-equilibrium	Al alloys p	roduced by	RTIL.	The pitting	g potential	was determir	ed using
potentiodynamic	polarization. 7	The testing solution	n is provided in	column "	electrolyte."					

Alloy	Alloying content (at%)	Electrolyte	Pitting Potential (mV _{SCE})	References
Al–V	9.1	0.1 M NaCl near neutral	-465	48
Al–Mo	9.8	0.1 M NaCl near neutral	44.9	49
Al–Zr	9.7	0.1 M NaCl near neutral	-377.6	50
Al–Mn	26	0.1 M NaCl pH 10	-265	51
Al–Ti	15.7	0.1 M NaCl near neutral	-301.9	52
Al–W	1.9	0.1 M NaCl near neutral	-345.1	53

detrimental effect. Pitting potentials for the Al alloys produced by high-energy ball milling are presented in Table V. The alloys were shown to exhibit high pitting potential along with the strength as represented by the hardness measurements. A figure showing simultaneous improvement in the ball milled alloys and comparison with the commercial alloys is presented in Fig. 2.⁶⁰ High strength and corrosion resistance of these alloys was attributed to the far from equilibrium microstructure consisting of grains <100 nm in size and high solid solubility of the alloying elements. High solid solubility of the alloying elements was attributed to the cause solid solution strengthening and improve the passive film stability.⁶⁰

Proposed Corrosion Mechanisms For the Improved Corrosion Resistance of Metastable Al–M Alloys Produced by Non-Equilibrium Aluminum Techniques

Corrosion of passivating alloys in the halide-containing environment is still the subject of debate.^{5,61–63} It is known that chloride ions (Cl⁻) induce passivity breakdown of otherwise thermodynamically stable oxide films. However, a specific mechanistic explanation regarding the interaction of (Cl⁻) with the passive layer has not been agreed upon. A general sequence of events would include an initial step where chloride ions are adsorbed onto the passive film, a secondary step where Cl ions interact with the oxide layer whether by penetrating it,^{64,65} thinning it^{66,67} or accelerating the formation and accumulation of point defects,^{44,68} a third step where the substrate metal becomes exposed in the form of a metastable pit, and final step where the metastable pit contains a sufficiently aggressive local environment preventing repassivation and allowing it to grow.^{69,70} Many models, expanded upon or modified version of these steps, providing detailed descriptions supported by experimental evidence have been proposed.^{44,66,67} These models have been reviewed extensively.^{5,61,62,64,71–73}

This section focuses only on the proposed mechanisms to explain the electrochemical behavior and surface chemistry of the supersaturated, non-equilibrium Al alloys. The nature of each alloying element and, therefore, influence on the corrosion properties would



Figure 2. Pitting potential (a representative of pitting resistance) versus Vickers hardness (a representative of yield strength) plot showing a simultaneous improvement in corrosion performance and strength of ball milled Al alloys whereas a decrease in corrosion performance with strength is observed in commercial alloys.⁶⁰

be unique. Furthermore, the solute quantity and accompanying microstructure for a given solute element would vary. There is no reason to believe that one single mechanism should satisfy the passivity of all non-equilibrium Al alloys, and therefore, a comprehensive understanding of all the possible mechanisms is essential.

pH of zero charge: delineating stability of the passive film.— The corrosion resistance of the Al alloys depends upon the stability of the surface oxide film in the chloride-containing environment. pH of zero charge model was posited to explain the stability of metal oxides in chloride environments.⁷⁴ The model is based on the idea

Table V. Pitting potential of high-energy ball milled Al alloys. All the tests were performed in 0.01 M NaCl solution in near neutral pH. The alloys were produced by HEBM followed by cold compaction. In situ consolidated alloys were in the form of small solid chunks produced directly from the HEBM process.

Alloying content (at%)	Processing	Pitting Potential (mV _{SCE})	References
11.5	HEBM/SPS	-280	3
5.5	In situ consolidation	-330	59
2.7	In situ consolidation	-360	59
1.0	0.1 M NaCl pH 10	-450	59
5	HEBM/cold compaction	-169	60
5	HEBM/cold compaction	-303	60
5	HEBM/cold compaction	-46	60
5	HEBM/cold compaction	-120	60
5	HEBM/cold compaction	-202	60
5	HEBM/cold compaction	-128	60
5	HEBM/cold compaction	-144	60
5	HEBM/cold compaction	-496	60
	Alloying content (at%) 11.5 5.5 2.7 1.0 5 5 5 5 5 5 5 5 5 5 5 5 5	Alloying content (at%)Processing11.5HEBM/SPS5.5In situ consolidation2.7In situ consolidation1.00.1 M NaCl pH 105HEBM/cold compaction5HEBM/cold compaction	Alloying content (at%)ProcessingPitting Potential (mV_{SCE})11.5HEBM/SPS -280 5.5In situ consolidation -330 2.7In situ consolidation -360 1.00.1 M NaCl pH 10 -450 5HEBM/cold compaction -169 5HEBM/cold compaction -303 5HEBM/cold compaction -120 5HEBM/cold compaction -120 5HEBM/cold compaction -120 5HEBM/cold compaction -128 5HEBM/cold compaction -144 5HEBM/cold compaction -144

that a surface oxide can attract Cl^- ions by two main attractive forces: coulombic forces and induction of the adsorbent by the approaching ion.⁷⁵ Electrostatic polarization of the ion and non-polar Van der Waal forces may also play a role.⁷⁶ Thus, the ionic nature of these attractive forces favors the adsorption of chloride ions when the surface is positively charged.

McCafferty et al. provided evidence that the outermost surface of oxide is covered with a layer of hydroxyl groups in the form of -MOH,^{77,78} where M refers to a metal cation and the hyphen represent its original bond to the oxide structure. In aqueous solutions, these hydroxyl groups will remain undissociated at the pH of zero charge. However, if the pH of the electrolyte is lower, the hydroxyl group -MOH will react with H⁺ ions forming $-MOH_2^+$, charging the surface positively. If the pH of the electrolyte is higher than the pH of zero charge, -MOH will react with OH^- forming $-MO^-$ species plus water,^{77,78} thus charging the surface negatively.

It is generally accepted that an initial step of chloride attack is the adsorption of the anion onto the surface of the oxide film. The pH of zero charge model states that surface oxides with pH of zero charge higher than the pH of the electrolyte in which they are immersed become positively charged. Therefore, Cl⁻ ions become electrostatically attracted, facilitating adsorption. This model suggests that alloys forming oxide films with a lower pH of zero than the electrolyte, their net surface charge will be negative when immersed in it. Thus, oxides such as Nb₂O₅ and Ta₂O₅ (pH of zero charge is 4.1⁷⁹ and 2.9,⁸⁰ respectively) have a net negative charge in near-neutral chloride containing environments. This negative surface charge will repel Cl⁻ ions electrostatically and prevent their adsorption to the oxide layer.

Natishan et al.⁷⁴ predicted that adding alloying elements that could form oxides with lower pH of zero charge than that of $Al_2O_3^{77}$ would lead to a much higher resistance to pitting corrosion in chloride environments, provided these alloying elements were in solid solution and did not form secondary phases. Indeed ion implantation of elements that formed oxides with low pH of zero charge such as Nb, Ta and Si exhibited considerable improvement in corrosion resistance.²⁴

A compendium of values of pH of zero charge for various oxides can be found in.^{23,24} A trend was found between the pitting potential and the pH of zero charge of the solute element oxide.²⁴ However, a direct relationship was challenging in ion-implanted alloys since they had variable chemistry despite applying the same accelerated voltage and ion dosage. It was believed that the mixed oxide layer would shift their pH of zero charge approximately proportional to the molar fraction,⁸¹ although other studies suggest that a simple molar fraction dependency is insufficient to explain the shift in pH of zero charge.^{31,32} Most notably, this has been pointed out in type 316 L stainless steel, whose pH of zero charge is lower than its constituent alloying elements.⁸²

With the technological advancements in processing and control provided by RF sputter deposition, the passive structure of nonequilibrium Al alloys was extensively characterized. Studies on XPS, ^{38,40,43,45} EXAFS⁴² and XANES^{51,83,84} provided significant insight on the chemistry and structure of the formed passive oxide film. Researchers expected a mixed oxide layer containing Al and solute cations. To their surprise, the amount of oxidized solute element was much smaller than it was on the alloy for most cases. ^{38,40,42,43,45,51,83–85} Either by preferential oxidation of the Al metal^{40,85} or preferential dissolution of the solute oxide, ⁸⁴ it was clear that the content of oxidized solute in the passive layer was insufficient to cause a substantial shift in the pH of zero charge. Additionally, Roy and Furstenau showed that at smaller solute concentrations, the pH of zero charge could have a variable or null dependency to the solute contents.⁸⁶

It should be noted that sputter-deposited Al alloys immersed in highly acidic conditions do exhibit considerable enrichment of the solute element in the passive layer.^{87,88} Thus, at affected zones, localized enrichment could take place, modifying the pH of zero charge only at affected locations by small quantities of oxidized

solute. This localized enrichment may come from the preferential release of Al^{3+} due to higher solubility than the solute inside of the pit solution.⁸⁹ Nonetheless, as much as the pH of zero charge model cannot be dismissed, passivity and corrosion resistance of non-equilibrium Al alloys may require more than pH of zero charge considerations alone.

Alloys producing inhibiting species: the release of inhibitors as corrosion occurs.—Hexavalent chromate is a well-known inhibitor of pitting corrosion in Al alloys.^{90,91} It has been widely used in conversion coatings until they were eventually discontinued due to environmental and health concerns.^{92,93} Other inhibitors have been investigated to replace hexavalent chromium with mixed results. For example, the efficiency of vanadates to inhibit localized corrosion may approximate that of hexavalent chromium⁹⁴ as long as it avoids polymerization into deca-vanadate.⁹⁵ Extensive work has been reported for the use of the inhibitors in coatings and electrolytes. However, the concept of alloys that contain inhibiting species within themselves has not been studied much.

Moshier et al. noticed that the electrochemical behavior of sputter-deposited Al-Mo alloys resembled that of pure Al immersed in the same solution with added molybdate inhibitor.³⁶ Molybdateassisted passivity in Mo-containing stainless steel had been suggested in the past.⁹⁶ Shaw et al.⁹⁷ used an anodization treatment in pure Al immersed in Na₂MoO₄ solution to directly incorporate molybdate inhibitor in the passive film of the pure Al. This treatment showed outstanding success, a clear ennoblement of \sim 500 mV in the pitting potential was found. However, despite their similar electrochemical behavior, XPS analysis revealed significant differences in the passive film chemistry of Molybdate-treated Al and sputterdeposited Al-Mo alloys. The passive film of molybdate-treated Al contained a large quantity of Mo⁴⁺ and Mo⁶⁺ species, in contrast with the sputter-deposited Al-Mo that only exhibited traces amounts of oxidized Mo. It appeared that the protection mechanism acting on molybdate-treated Al was solely due to the action of trapped inhibitor ions and that the non-equilibrium Al-Mo alloy might achieve comparable corrosion resistance by the effect of something else.

The idea of an alloy that contains inhibiting species was explored in sputter-deposited Al–Co–Ce.⁹⁸ CeCl₃ and CoSO₄ had been proven to be potent inhibitors.⁹⁹ Non-equilibrium Al–Co–Ce alloys was used to coat a commercial Al alloy.⁹⁸ It was observed that the release of Ce ions was pH-activated and provided inhibition on affected zones, where accelerated dissolution and hydrolysis of Al³⁺ would take place. Once Ce ion inhibition took place, Al³⁺ production rates decreased, and the pH would return to normal, moderating the further release of Ce inhibiting ions.¹⁰⁰

Not only could Ce^{3+} and Co^{2+} act as inhibitors, but other metal cations like Fe^{2+} , Ni^{2+} , Y^{3+} , Pr^{3+} , Nd^{3+} , and La^{3+} have significant efficiency in inhibiting corrosion of aluminum alloys in chloride environments.¹⁰¹ Cationic protection is a concept that has been modestly explored but could expand the capabilities of inhibitor-containing alloys in the same manner as Al–Co–Ce alloy. With further development of non-equilibrium alloying techniques, the addition of these elements that can prompt controlled-released cation inhibition and present a promising field for further exploration.

Recently, Gupta et al. prepared inhibitor-containing aluminum by directly adding inhibitor as starting material for a high-energy ball milling production process.¹⁰² The inhibitor is finely and uniformly dispersed throughout the entire bulk of the alloy, and it releases as corrosion initiates. This concept exposes the capabilities of high-energy ball milled alloys containing agents that inhibit corrosion.

The concept of inhibitor release becomes of particularl interest in the case of localized corrosion, where a significant amount of metallic ions are released in a confined space. This concept has not been explored in great detail and deserves careful experimental as well as analytical attention. The results on Al–M alloys needs to be revisited with progress in understanding of pitting mechanisms and advancements in experimental, analytical and modeling tools. Role of inhibitor species generated within the pits may be different than the effect of inhibitors by adding the bulk electrolyte. Studying the corrosion mechanisms and formation of various ions during corrosion in simulated critical pit solution would be useful in developing further insight.

Solute-vacancy interaction model (SVIM): controlling the point defect density in the passive film .- An atomistic sequence of events that explained passivity and oxide film breakdown was envisioned in the point defect model (PDM)^{68,103} proposed by Macdonald and coworkers. The PDM model assumes that the principal entities involved in oxide growth are Schottky-type of defects. 68,103 These entities are the point defects present within the oxide structure, most notably, cation vacancies, anion vacancies and cation interstitials. These point defects are charged species generated at either the electrolyte/oxide or the oxide/metal interface. The PDM states that if they are generated at the former interface, they will be transported to the latter interface to be annihilated at a given rate. If the rate of generation of defects is faster than their rate of diffusion or annihilation, accumulation will occur. The PDM predicts that accumulation of cation vacancies at the metal/oxide interface leads to the collapse and breakdown of the passive oxide film.

An expansion of the point defect model was proposed to account for the role of minor alloying elements such as Mo and W in stainless steel.⁴⁴ This model was called the Solute-Vacancy Interaction Model (SVIM). Even to this day, there is no agreement on the role of Mo and W in improving the corrosion resistance of stainless steel.^{5,73} Nonetheless, the SVIM proposes that minor alloying additions like Mo are present in their maximum oxidation state (Mo^{6+}) within the passive film. This cation has a high positive charge and can interact with several cation vacancies of low negative charge. The result would resemble complex species of neutral charge and null mobility. Thus, Mo^{6+} would consume cation vacancies preventing them from accumulating at the metal/oxide interface. The SVIM was constructed using the concept of solute ion/vacancy equilibrium constants, which can be estimated using the ion-pairing theory¹⁰⁴ and the Debye-Huckel theory.¹⁰⁵

Despite its relatively simplistic nature, the SVIM was considerably accurate in predicting both pitting potential and induction times in Fe-17Cr and Fe-18Cr¹⁰⁶ stainless steels. Similarly, The SVIM could explain the passivity of non-equilibrium Al alloys, and the idea has been suggested in the past.¹⁰⁷ The SVIM model could be applicable considering the semiconducting nature of the oxide film found in non-equilibrium Al alloys. Typically, the semiconducting properties of oxide films formed in pure Al and its alloys show that the passive films resemble a n-type semiconductor.^{108,109} However, oxide modification by co-sputtering Cu-Al-O produced a p-type semiconductor,¹¹⁰ where the preponderant defects are cation vacancies.^{11,112} XPS^{38,40,43,45,85} and EXAFS⁴² studies revealed that passive oxide film in non-equilibrium Al alloys consisted of predominantly of an aluminum oxide-hydroxide layer with traces amount of the oxidized solute element. These traces of oxidized solute, well-dispersed throughout the film, are the most notable difference in the chemistry of the surface oxide compared to that of regular Al alloys. A switch in semiconducting behavior, from n-type to p-type indicates that the process is now limited by transport of cation vacancies, and passivity breakdown occurs by the accumulation of cation vacancies at the metal/oxide film interface. As such, highly oxidized species such as Mo⁶⁺, V⁵⁺ and W⁶⁺ would be capable of stifling the process. However, the SVIM assumed that the content of Mo⁶⁺ in the passive layer is proportional to the amount of Mo in the bulk of the alloy, and considering different oxidation states, or a mixture of them, deviated the predicted values from experimental results. This is in contrast with XPS results on sputterdeposited alloys showing a multitude of oxidation states and much lower oxidized solute quantities. Nonetheless, SVIM is a robust deterministic model that can provide insight and work as a foundation for further studies. Studying the SVIM for a wide range the alloys, mainly alloys produced by nonequilibrium methods,

would be beneficial in understanding the corrosion mechanisms and role of alloying elements on the characteristics of the passive film.

Solute rich interface model (SRIM):): changing the composition of the passive film .-- Solute elements that form solid stable oxides at a wider range of pH than aluminum were taken into high consideration as design criteria in non-equilibrium Al alloys. 39,40,43,45 Elements such as W, 113 Mo, 114 Cr, 115 and Ta¹¹⁶ are passive in acidic pH and can protect by forming a protective oxide layer on the surface. Cr induced passivity in austenitic stainless steel is a classic example of this phenomenon. Cr and Fe oxides may be stoichiometric to the bulk composition in an initial step. However, in acidic environments, Cr oxide persists while Fe oxide is preferentially dissolved.¹¹⁷ The preferential dissolution of a single element from the bulk material may also cause a chemistry change at the outer-most section of the substrate underneath the oxide. In the case of the aforementioned austenitic stainless steel, a Ni-rich metal layer is formed between the oxide and the bulk, giving origin to the three-layer model.¹¹⁷ Surface characterization studies in stainless steels have been extensively reviewed.7

A similar phenomenon, dealloying, was observed in Cu-Zn alloys.¹¹⁸ Dealloying has been described by Pickering¹¹⁹ and several other researcher, such as the percolation theory^{120,121} and the graph theory.^{122,123} In particular, Pickering classified types of selective dissolution in binary alloys (A-B) and proposed that the difference in standard reduction potential ΔE° between A-B determines the type of selective dissolution.¹¹⁹ When component B is significantly more noble than A, a metal (B) rich diffusion layer is formed, and the electrochemical behavior, as observed by the different regions in a polarization plot, depends strongly on the thickness (δ) of the diffusion layer. This metallic diffusion layer was hypothesized to decrease in thickness with increasing potential until the oxidation potential of B is reached, though a thin, nano-sized layer would still be enough to protect the alloy as long as there is full surface coverage. Considering the difference in standard reduction potential between Al and some of the alloying elements of non-equilibrium Al alloys, this principle could be applied for non-equilibrium Al alloys of the form Al-M.

Similarly, Davis proposed a solute rich interface model (SRIM) to explain the passivity of Al–W⁴⁰ and Al–Ta⁴⁵ alloys after careful and exhaustive surface characterization studies. Previously, it was suggested that solute elements might act directly at the active pit surface rather than the passive film,⁸⁹ the acidic environment of a metastable pit would have to overcome the solubility of the solute metal over the precipitation of the solute metal oxide.^{16,89} Similarly, the SRIM model proposes that solute metal enrichment would occur at a metastable pit site due to the preferential dissolution of Al. This solute, rich region, would inhibit pit initiation and stabilizing occulted cells.⁴⁰ Further, if high dissolution rates and acidification take place, W in both the alloy and passive film increases, providing the affected zone with a more stable W oxide passivating the site.⁸⁹

SRIM can explain the marginally low concentrations of oxidized solute in the passive layer while expecting considerably larger content at lower pH.^{40,85,124} Indeed several studies in highly acidic environments were conducted on sputter-deposited alloys exhibiting clear enrichment of oxidized solute in the passive layer.^{46,124–127} More concrete evidence of a solute rich interface was provided by Principe & Davis using TEM analysis.⁸⁵ STEM images coupled with EDS elemental map analysis clearly show the appearance of W rich layer zones between the oxide and the bulk alloy. Furthermore, the existence of a solute rich interface was also supported by AC and DC studies.^{124,128} A similar concept to SRIM has been proposed by Hashimoto and coworkers where tungsten oxide "healed" affected zones preventing the rapid local dissolution of the alloy.^{46,125–127}

There is convincing evidence that supports SRIM.^{40,85,128} However, several questions remain unanswered. Firstly, if a tungsten rich interface alone is responsible for the improvement in corrosion resistance in Al–W alloys, then tungsten should improve the corrosion resistance of Fe^{129} as much as it does to Ni¹²⁹ or Al.⁴⁶

Apparently, W works in synergy with other elements that form passive oxide layers, whilst not being a passive layer former itself. Additionally, W contents exceeding 3 wt% have been shown to provide no further protection in stainless steels; hence the continuing debate over W assisted passivity. The role of a W-rich layer in improving corrosion resistance is unclear as long as the role of W itself remains unclear. The role of other alloying elements that improve corrosion resistance may find this complication as well.

Secondly, if a solute rich interface would eventually form, corrosion resistance of the alloy would have little dependency on the bulk composition, especially for the high solute contents. In contrast, some alloys exhibit monotonical ennoblement in the pitting potential with an increasing solute concentration in bulk.¹⁷

Thirdly, a solute rich interface is more evident in highly acidic environments. However, oxidation kinetics may be drastically different than they are inside a pit at neutral pH and chloride environment. Thus, the oxide/rich layer arrangement found at very low pH could not be directly extrapolated to what occurs during an active pit. Evidence of the metal-rich layer was found, though evidence of a W rich oxide actively protecting affected zones remains to be seen. Further research on the corrosion of nonequilibrium Al alloys in the simulated pit or pit-like solution would help in developing further mechanistic insight.

Controlled dissolution: facilitating repassivation in case of passive film breakdown.-Considerations on the role of anodic dissolution to pitting stability started with Galvele.⁷⁰ He proposed a one-dimensional pit model that described the transport of the species by diffusion generated from hydrolysis of metal cations. This model correlated well with experimental observations and suggested that the main reason for passivity breakdown at initial stages of pit growth was localized acidification. He introduced the concept of x^{*i} ,⁷⁰ where i is the current density of the bottom of the pit, and x is the pit depth. At a given x*i value, the pH drops enough that stable dissolution takes place (e.g., 10^{-4} A m⁻¹ for Fe). Thus, as long as the current density is large enough to hydrolyze the environment, and the pit is deep enough to prevent the acidic environment from escaping, stable pitting will occur. Additionally, he also considered the effect of chloride ions on the severity of the local environment and the pitting potential of the metal. It was later suggested that at high current densities, the ionic concentration reaches supersaturation, and thus, a salt film is formed inside of the pit.^{130,131} The process is subsequently controlled by diffusion through this salt film.^{132,133} Whether or not this film is necessary for pit growth is not clear.⁸⁹ However, this could act as a buffer that can readily provide cations to reconcentrate the pit solution if required.⁶

The Galvele model and considerations of dissolution rates and depth to form stable pitting are still relevant.^{134,135} However, the concept of controlled dissolution by the effect of alloying elements was suggested by Newman^{136,137} while investigating the role of minor additions of Mo on corrosion of Fe–Cr alloys. He studied anodic current densities during the active dissolution of scratched¹³⁶ and artificial pits¹³⁷ in Fe–Cr and Fe–Cr–Mo alloys in HCl and observed a clear decrease in the pit current density suggesting that Mo directly alters dissolution kinetics. A decrease in the anodic dissolution rate directly decreases the x*i parameter, retarding the pitting corrosion. More extensive reviews on the role of Mo in corrosion of nickel alloys¹³⁸ and stainless steel¹³⁹ have been done. However, there seems to be the notion that Mo influences dissolution kinetics and pit growth.⁶ A similar effect has also been suggested for the role of N is stainless steel.¹⁴⁰

Similarly, controlled dissolution in non-equilibrium Al alloys was suggested as the potential mechanism of enhanced corrosion resistance.¹⁷ A passive film enriched with the solute may not be required on all the surface at neutral pH. However, enrichment of the solute in the surface film in low pH conditions, such as inside the pit or crevice, would occur and enhance the corrosion resistance. The surface characterization studies performed after the electrochemical tests in neutral solution did not observe significant enrichment due to

the larger area of the surface being analyzed and the solute enrichment to be localized within the pits. The observed enrichment of oxidized solute in the passive film at highly acidic pH conditions supports the proposed concept of surface enrichment within pits as a potential corrosion protection mechanism. Recently, it has been suggested that designing alloys with controlled dissolution i.e., alloys, where the rate-controlling step is active dissolution during pit growth rather than more stable passive oxide films, is a better strategy for the aggressive environments.¹⁴¹

Passivity promoters and dissolution blockers: explaining the influence of the alloying elements on the passive film formation and repassivation.—This model was based on the utilization of metallic binding energies in explaining the corrosion resistance of metals and alloys. Metal-to-metal bond strength was proposed as a major contributor to the corrosion mechanism by Marcus¹⁴² and Okazaki.¹⁴³ Marcus, additionally proposed that Metal-to-oxygen bond strength played a major role as well. Okazaki observed that the strong covalent bond energy that Ti has with elements like Nb and Zr in solid solution would decrease metallic dissolution rates. This was used to explain alloying additions to Ti in simulated physiological solution¹⁴⁴ and hydrochloric acid.¹⁴⁵ The apparent increase in covalent bond strength was attributed to the electronic structure of these elements.^{144,135} A similar approach was used to explain corrosion rates of Ti with Nb and Zr additions while also considering surface enrichment effects by the preferential dissolution of Ti.¹⁴⁶

Marcus¹⁴² classified the beneficial alloying elements into two categories: passivity promoters and dissolution blockers. He did this by analyzing the metal-to-metal and metal-to-oxygen bond strength. Passivity promoters were defined as those that have a high affinity to recombine with oxygen and a small tendency to remain in metallic bonds. The combination of these two was deemed a crucial factor for the nucleation of oxide, allowing it to form a three-dimensional protective oxide film rapidly. Moreover, dissolution blockers are those that have high metal-to-metal bond strength and also high metal-to-oxygen bond strength. These elements alone cannot rapidly form a 3D oxide film. However, they react more slowly while not being detrimental to the overall passivity. All of these factors are in agreement in the context of what was discussed previously, where one of the reasons during early pitting formation was acidification caused by local fast anodic kinetics.

The thermodynamic representatives of metal-to-oxygen and metal-to-metal bond strength are the heat of adsorption, $\Delta H_{ads}(ox)$, and the metal-metal bond energy, ε_{M-M} , respectively. Marcus plotted these two properties and identified elements like Al, Ti, and Cr as passivity promoters whilst other elements like Mo, Nb, Ta and W as dissolution blockers. Extended thermodynamics and surface property data has been reported.¹⁴⁷ This was a straightforward but practical approach to explain the passivity of stainless steel by additions of Cr, while also explaining the synergistic effect of minor elements like Mo and W.¹⁴⁸ Cr was required to provide passivity to Fe, while Mo and W facilitate repassivation on the event of passivity breakdown.

One could extrapolate this concept to Al. Al is an already passivating material with low $\varepsilon_{\rm M-M}$, and high $\Delta H_{\rm ads}(ox)$ that could be significantly benefited by additions of Mo, Nb, and W. These elements have limited solubility in Al and tend to form detrimental intermetallics. However, their addition by non-equilibrium techniques has resulted in outstanding improvement, as seen in sputter-deposited Al–Mo, 41 Al–Nb, 17 and Al–W 39 alloys. Furthermore, adding Cr and Mo simultaneously further improves corrosion resistance even at the most acidic conditions. 87 Considering Cr as an additional passivity promoter known to form well-adherent and well-compacted oxide films. 73

This model is consistent with most experimental observations in non-equilibrium Al alloys, though it remains imprecise. The bond energy between two metals where one is a substitutional solute atom would differ from that of the bond energy of pure metals. This



Figure 3. (a) Back scatter electron image of an Al–20Cr alloy produced by high-energy ball milling. Alloy contained bright Cr rich particles and a Cr rich matrix, denoted as I, and a Cr lean region denoted, as II. (b) High annual angular dark field image of the Cr rich matrix (I) showing Cr rich regions (III), Cr lean regions (IV) and unalloyed Cr particles (V).³

creates a large dependency of the elements used in the alloying system and could drastically change the position of some alloying elements in Marcus' diagram. Simulations on electronic and structural properties of solid solutions in binary alloys can be performed using the density functional theory.¹⁴⁹ These may be extrapolated to supersaturated solid solutions, though the effect of a significantly high solute content remains to be accounted for.

Heterogeneous microstructures and importance of understanding corrosion mechanisms at various length scales.—The mechanisms described in the previous sections were primarily proposed to explain the influence of the solute when present in solid solution, which has been observed in sputter-deposited alloys. Heterogeneities in the form of secondary phases are deemed deleterious to the corrosion resistance. However, recent studies on the high-energy ball milled Al alloys^{3,59,60,150} and heat-treated sputter-deposited Al alloys,^{39,151} which contain supersaturated solid solution with uniformly fine distributed phases, have also shown improved corrosion resistance. For instance, an Al-20Cr alloy produced by high-energy ball milling contained three main phases: 1) matrix rich in Cr, 2) Cr lean phases distributed in the matrix, 3) unalloyed Cr rich particles (Fig. 3a).³ High-resolution TEM analysis on the matrix indicated uniform distributed of Al-Cr solid solution and Al-Cr intermetallics (Fig. 3b).³ Despite of a heterogeneous microstructure, Al–20Cr alloy exhibited high corrosion resistance which indicated the controlled heterogeneity can be used in designing corrosion resistant alloys. Precise corrosion mechanisms for this alloy are not well understood; one or more of the above-mentioned mechanisms should be applicable. The high corrosion resistance of heterogeneous Al alloys indicated the significance of understanding corrosion mechanisms at various length scales. Further research on understanding the corrosion mechanisms of such alloys would help determine the corrosionresistant microstructure and development corrosion-resistant Al allovs.

Surface film of the corrosion resistant alloys as studied using XPS data has shown presence of only trace amount of solute in the passive film (Table III). Doping of the oxides with impurities, such as Cr^{3+} addition to Al_2O_3 , has been shown to have strong influence on the characteristics of the oxides.^{152,153} Possibility of the occurrence of similar phenomenon in corrosion resistant Al alloys, i.e., significant change in the passive film characteristics due to the doping of the solute cannot be overruled. Therefore studying the oxide film structure warrant further attention to develop fundamental understanding and develop corrosion resistant alloys. Studies focused on the role of the solutes ions on the passive film structure, point defect density, binding energies, and dissolution would be

helpful. Moreover, role of dissolved gases and impurities on corrosion behavior has attracted only limited attention. Frankel et al.¹⁵⁴ showed that the oxygen content in the sputtered Al films had a significant influence on the corrosion behavior. Detailed studies using advanced alloy and surface characterization tools in combination with modern electrochemical and simulation methods will lead to complete understanding of the corrosion behavior of the corrosion resistant Al alloys.

Concluding Remarks

The mechanisms proposed for the improved corrosion resistance of Al alloys produced by the non-equilibrium processing methods have been presented. Selected solute elements like Cr, Mo, V etc have been shown to improve the corrosion resistance even present in small quantities (\sim 1 at%). The mechanisms, based on both structural and chemical considerations of the passive oxide film and the substrate metal, were complementary to each other. A combination of several mechanisms is more likely to co-occur. Applicability of the one or combination of the proposed mechanisms would depend upon the nature and content of the solute alloying element. Further, in-depth studies are needed for a complete understanding of the high corrosion resistance of these alloys, which would lead to better alloy design criteria, appropriate and practical selection of the synthesis and processing techniques, and surpass the current property limits of Al alloys regarding corrosion behavior and mechanical properties.

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Data availability statement

The data presented herein is extracted from the open scientific literature and the source of the data is cited as appropriate.

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