MSD Materials Selection & Design

Corrosion of Naval Aluminum in Seawater

A. Eliezer and J. Haddad, *Sami Shamoon College of Engineering, Israel*
A. Garcia, B. Valdez, and M. Schorr, *University of Baja California, Mexico*

The corrosion of naval aluminum alloy UNS A95052 was investigated by exposing specimens in seawater at two ports—Ensenada on the Pacific Ocean, Mexico, and Ashdod on the Mediterranean Sea, Israel. Corrosion rates were calculated from weight loss and electrochemical parameters were measured in laboratory simulation tests. The alloy displays adequate corrosion resistance to both seawaters.

Aluminum is a light metal that helps to reduce weight in all types of vehicles—aircraft, cars, trucks, railway wagons, naval vessels, and research and rescue submarines—and consequently saves fuel and reduces the cost of vehicle operation. The affinity of Al for oxygen is responsible for its great stability and its resistance to corrosion. Al exposed to air is covered with a thin impervious film of protective oxide (aluminum oxide [Al_2O_3], or alumina) with varied thicknesses (5 to 10 nm) that can also be generated by anodic oxidation in appropriate electrolytes. In addition, magnesium in the Al-Mg alloys is converted into a hard, tenacious oxide, magnesium oxide (MgO), or magnesia.[1]

Al is not affected by changing climatic factors such as humidity, heat, or slight acidification of the sea by dissolution of carbon dioxide (CO_2) and other greenhouse gases. Al-made equipment (land, space, and marine) is exposed to two basic environments: water bodies, fresh or salt, and the atmosphere for buildings and aircraft at different altitudes and humidities. Its low cost, favorable machinability and weldability, propitious thermal and electrical properties, and nontoxicity make it attractive for many applications.

This work is the result of an international cooperation between the Universidad Autonoma de Baja California, Mexico and the Sami Shamoon College of Engineering, Israel.

Seawater

Seawater consists of a solution of many salts and numerous organic and inorganic particles in suspensions. Its main characteristics are salinity and chlorinity; and, from the corrosion point of view, dissolved oxygen (DO) content, which ranges from 4 to 8 mg/L depending on temperature and depth. The ocean's surface salinity is determined by the bal-

TABLE 1
Seawater and river water chemical composition

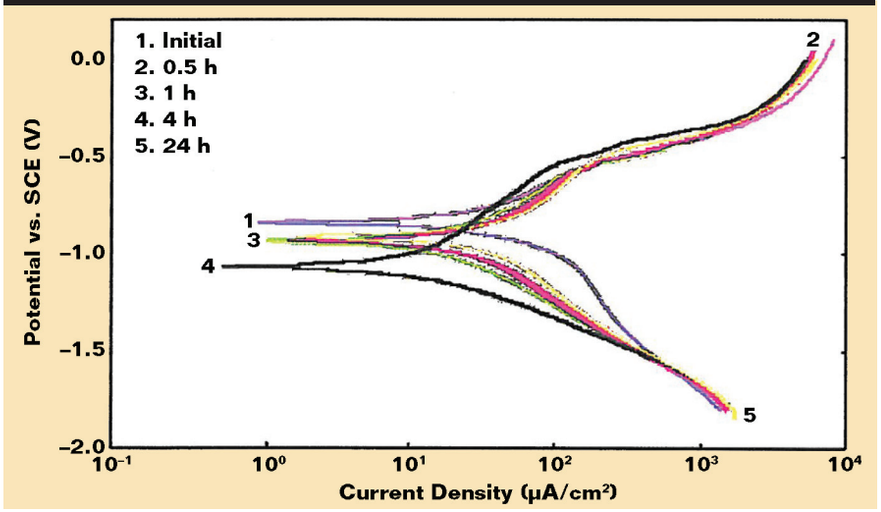
Component	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	SiO_2	EC	Salinity
Sea (g/L)	10.7	0.4	1.3	0.41	19.3	0.14	2.71	—	50 to 60	3.5%
River (mg/L)	6.3	2.3	4.1	15.0	7.8	58.4	11.2	10	2 to 5	—

ance between water lost by evaporation and gained by precipitation. The salt concentration, particularly sodium chloride (NaCl), varies from 2.0 to 3.5%, according to the sea location and the massive addition of fresh river water. For instance, in the Red Sea—an enclosed basin with high summer temperatures—salinity is 4.1%. At the Baltic Sea, however, salinity is ~2.0% since many rivers feed into it.

Seawater is slightly alkaline, with a pH of ~8.0. When it is contaminated by acids, such as in coastal regions near power stations where burning fossil fuels generate acidic rains, the pH can diminish to 5.

Table 1 shows the different salt content of sea and river water and the consequent dilution effect of river water when emptying into the sea. The sea is a dynamic system in constant motion, with complex surface currents. Winds blowing over its surface generate waves and tides that reach the coast and its facilities and installations. The sea phenomena vary during the course of the year and its seasons and with the vagarities of wind and weather. In splash zones, violent waves break down with whitish, oxygenated foam, increasing local corrosion.[2-3]

FIGURE 1



Polarization plots for A95052 in Ensenada seawater under stagnant conditions.

Naval Vessels

The first wooden sailing vessels were built by the Phoenicians, a seafaring people located on the Mediterranean Sea shore (now Lebanon), who established maritime navigation and commerce along the Mediterranean coast. Nowadays, ships are made mainly of steel but protected against corrosion by marine coatings and cathodic protection (CP).

Ship corrosion is synonymous with marine corrosion, since a ship is subject to all forms of marine corrosion. A ship navigating the open sea has three areas that are exposed to diverse environments and corrosive conditions—the underwater hull, which is submerged in seawater, often covered with marine fouling, and supplied with plentiful oxygen; the deck area, which is exposed to sweeping waves, salt spray, and heated by solar radiation; and the superstructure, which includes the sailor quarters, chimneys, and masts that support communication equipment. Acidic exhaust fumes from the ship's electricity-producing facilities, wind-driven salt water, and condensation on cold nights are factors that increase the corrosion attack. Different types of paints and coatings are applied to these areas of the ship.

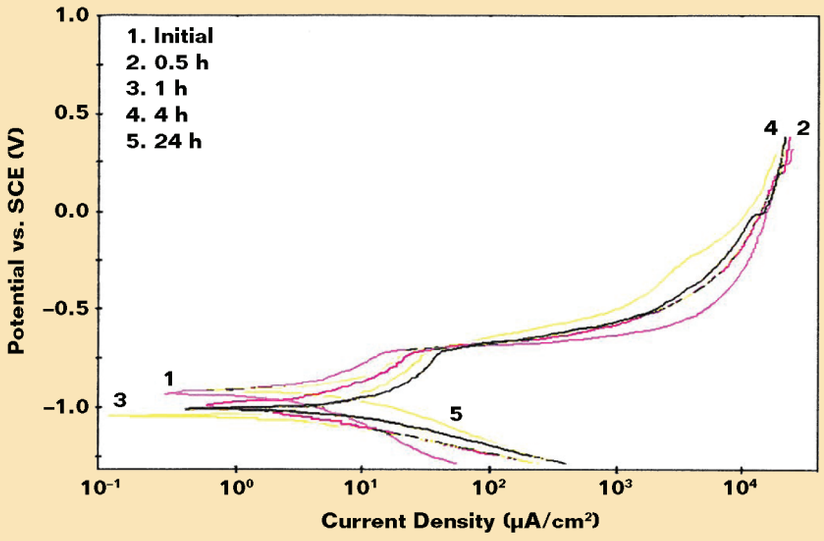
Fast, light, small seagoing vessels used for military action; interdiction of pirates, terrorism, and smuggling; and search and rescue operations are constructed from naval Al of the 5xxx series in which Mg is the principal alloying element. Al and Mg form solid solutions over a wide range of composition, a structure that promotes corrosion resistance. In steel-hulled ships, the superstructure is built of Al-Mg alloys. The masts, booms, and fitting of sailing boats are made of anodized Al.[4] Experts familiar with ship construction and marine corrosion have proposed to replace steel with Al alloys in the shipbuilding industry to reduce the ship weight and save fuel.[5]

Aluminum Corrosion

Reflecting its amphoteric nature, Al corrodes under both acidic and alkaline conditions, yielding Al^{3+} ions and AlO_2^- aluminate ions, respectively. In seawater with a pH of ~8, the dominant corrosion factor is the DO concentration. When Cl^- penetrates the passive film, it initiates pitting and crevice corrosion at localized sites with breakdown of passivity.[6-8]

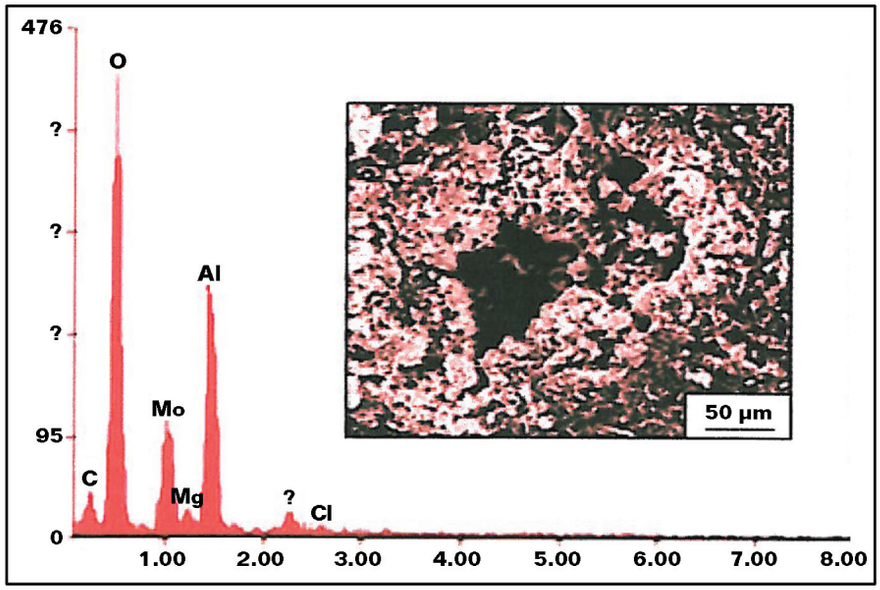
The electrochemical corrosion mechanism of Al alloys is explained by its anodic and cathodic reactions:

FIGURE 2



Polarization plots for A95052 in Ashdod seawater under flowing conditions.

FIGURE 3



SEM micrograph and EDX results of A95052 after exposure in Ensenada seawater under flowing conditions.

$$2\ Al \rightarrow 2\ Al^{3+} + 6e^- \quad (1)$$

$$3\ H_2O + 1.5\ O_2 + 6\ e^- \rightarrow 6\ OH^- \quad (2)$$

$$2\ Al + 3\ H_2O + 1.5\ O_2 \rightarrow 2Al\ (OH)_3 \quad (3)$$

This hydroxide converts into a hydrated oxide (alumina, $Al_2O_3 \cdot 3\ H_2O$), strongly adhered to the Al surface. The Al potential, ~ −1.65 V (saturated hydrogen electrode [SHE]) indicates its natural tendency to corrode but the alumina oxide film imparts a passive condition and corrosion resistance for Al marine equipment in contact with seawater. In the intermediate pH range between 4 and 8, where Al_2O_3 provides a protective film, the corrosion rate is negligible. The regions of immunity, corrosion, and passivation for Al, as a function of pH and electrode potential, are depicted in the Al Pourbaix diagram.[1]

The regular corrosion rate for steel in seawater ranges from 0.1 to 0.3 mmy^{-1}, but can rise to 2 to 4 mmy^{-1} in seawater contaminated with corrosive effluents. The corrosion rate for A95052 in the same water is 0.05 mm/y.[9] Marine ports, shipyards, and the adjacent coastal zones are polluted sometimes by industrial, municipal, and agricultural wastes generated in the region. Rivers that flow into coastal waters discharge such effluents, which contain many corrosive and toxic chemically active pollutants. These pollutants increase the electrical conductivity of the water, and increase the extent of corrosion.[10-11]

Corrosion Testing

Electrochemical and gravimetric corrosion tests on A95052 were carried out in two environments. Samples were exposed in two ports—Ensenada, located on the Pacific Ocean in Baja California State, Mexico; and Ashdod, located on the Mediterranean Sea south of Israel. Samples were also exposed under stagnant and flow conditions in seawater brought from the two ports at the Corrosion Research Center, Sami Shamoon College of Engineering, Israel and at the Materials and Corrosion Laboratory, Universidad Autonoma de Baja California, Mexicali, Mexico. Test coupons were fabricated from a sheet of A95052 alloy of different dimensions that varied according to the exposure sites. The coupon surfaces were cleaned and tested in the "as-received" condition. For the gravimetric measurements of corrosion rates, the specimens were weighed, exposed to seawater, cleaned of corrosion products, and weighed again to determine their weight loss. These tests were conducted in accordance with the practices recommended in ASTM standards G1,[12] G4,[13] and G31.[14]

Potentiodynamic polarization plots were obtained following ASTM stan-

dards G3,[15] G5,[16] and G52[17] using a three-electrode cell (Al specimen saturated calomel electrode [SCE] reference, and auxiliary graphite electrode) and applying a software-controlled potentiostat. The plots are displayed as an electrode potential-current density (CD) relationship (Figures 1 and 2).

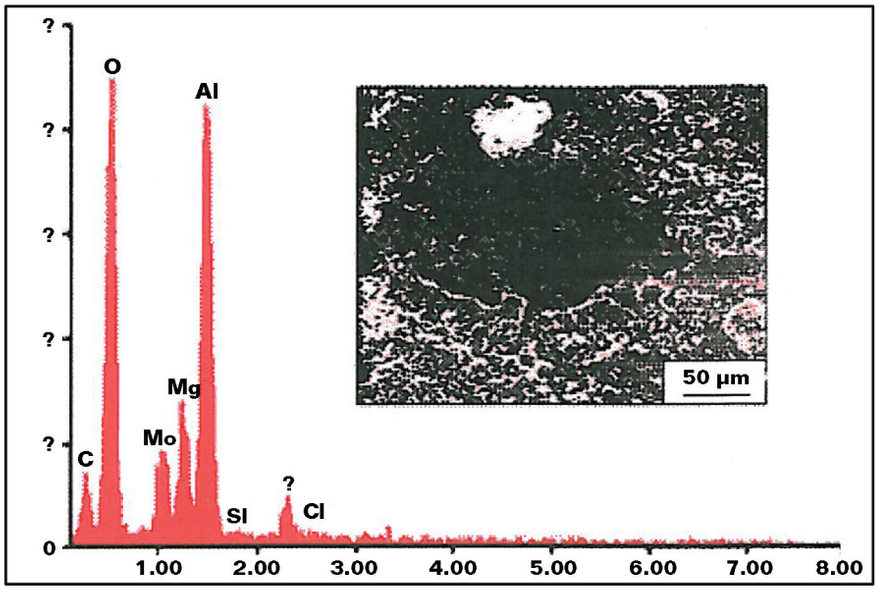
The surfaces of the test coupons were examined before and after exposure to seawater by scanning electron microscopy (SEM) to observe initial and final conditions of the surface and by energy dispersive spectroscopy (EDX) for elemental analysis composition (Figures 3 and 4).

Results

Table 2 presents results of immersion corrosion tests of unprotected A95052 based on measurements of mass loss and expressed as mm/y, in accordance to the practice recommended in ASTM standard G31. The corrosion rates (CR) in stagnant seawater are greater than the CR observed in flowing seawater where the protective Al_2O_3 film prevails. The CR was determined after 24 h of exposure to seawater at 25 °C. The results show similar CR values in both seawaters. The CR measured in the Ashdod Port Marina are greater than those obtained under laboratory conditions (Table 2). Table 3 displays the open circuit potential (OCP) of A95052 and other Al alloys measured in seawater vs. SCE. These negative potentials indicate corrosion activity, even if the alloys are protected by a thin oxide film. In the galvanic series in flowing seawater, Al alloys including A95052 are positioned in the active, anodic extreme of the series with values in a wide range, from −0.8 to −1.2 V (SCE). A similar behavior of the potential CD plots was observed in an investigation of Al alloy A96065 in 0.1 M NaCl with an OCP of −0.70 V.[18]

The electrochemical potentiodynamic polarizations (PP) anodic and cathodic plots depicted in Figures 1 and 2 are typical of an active metal. The potential run begins at the OCP potential with a scan rate of 10 mV/s, in the noble direction. At a more noble potential, a straight quasi-vertical line appears with a small change in CD that indicates a certain degree of passivity, in particular under flowing conditions with an abundant, uninterrupted supply of DO. There is no significant difference in the A95052 alloy potential under stagnant and flowing conditions in both seawaters. On the other hand, under flowing conditions, strong water circulation prevents the

FIGURE 4



SEM micrograph and EDX results of A95052 after exposure in Ensenada seawater under stagnant conditions.

TABLE 2
Corrosion rates of UNS A95052 in seawater

Seawater	Laboratory[A]	Condition	CR Range (mm/y)
Ashdod, Marina	—	Flow	1.25 to 1.75
Ensenada	II	Stagnant	0.58 to 0.68
Ensenada	II	Flow	0.11 to 0.53
Ashdod	CRC	Stagnant	0.60 to 0.70
Ashdod	CRC	Flow	0.24 to 0.020

[A]II: Institute of Engineering, University of Baja California, Mexico; CRC: Corrosion Research Center, Sami Shamoon College of Engineering, Israel, CR: Corrosion rate.

TABLE 3
OCP of UNS A95052 in seawater

Seawater (Condition)	Potential Range (V vs. SCE)
Ensenada (stagnant)	–0.8 to –1.2
Ensenada (flow)	–0.8 to –1.2
Ashdod (flow)	–0.9 to –1.0
Ashdod (stagnant)	–0.8 to –1.0

accumulation and adsorption of Cl^- ions on the alloy surface. The plots obtained from Ensenada and Ashdod seawaters are quite similar too. During the tests the seawater pH was quite stable, ~8.1.

Figures 3 and 4 show the elemental chemical analysis by EDX and the Al95052 surface features by SEM and illustrate localized pitting corrosion. The two elements with major concentration in the film are Al and O, which form the Al_2O_3 layer. Other elements are Mg, the alloying element, and Cl^- remaining from the seawater. Cracked corrosion products and some pits are observed on the alloy surface. Pitting corrosion may be intensified by the accumulation of hydroxyl ion (OH^-) inside the pits, with more alkaline solution.

Summary

Naval Al A95052 combines high mechanical properties, light weight, and improved corrosion resistance, making it a suitable material for construction of military and civil river and seagoing vessels used by navies of many nations.

The corrosion resistance is based on the presence of an Al_2O_3 film formed by reaction with the seawater DO, as shown by the EDX elemental analysis and the potentiodynamic polarization plots.

Acknowledgments

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JEHUDA HADDAD is the president of the Sami Shamoon College of Engineering, 84 Jabotinski St., Ashdod 77245, Israel. He is a pioneer of the development of high education in the Negev, south of Israel, as well as a founding member of the Sami Shamoon College of Engineering. Haddad is an expert in the field of aerospace and advanced materials in industry and has many international publications within this research area. Recently, he was appointed as the chair of the Engineering Colleges Association in Israel.

B. VALDEZ is the director of the Institute of Engineering, Universidad Autonoma de Baja California, Blvd. Benito Juárez y calle de la Normal s/n, Colonia Insurgentes Este. cp. 21280 Mexicali, Baja California, México. He has a B.Sc. in chemical engineering and a M.Sc. and a Ph.D. in chemistry, and is a member of the Mexican Academy of Science and the National System of Researchers in Mexico. He was the guest editor of *Corrosion Reviews*, in which he produced two special issues on corrosion control in geothermal plants and the electronics Industry. He is a full professor at the Universidad Autonoma de Baja California. His activities include corrosion research, consultancy, and control in industrial plants and environments. He has been a NACE International member for 20 years.

AMIR ELIEZER is the director of the Corrosion Research Center Nano-Bio & Advanced Materials, as well as a faculty member of both civil engineering and mechanical engineering at the Sami Shamoon College of Engineering, Israel. He is active as a NACE International Europe board member, World Corrosion Organization Board of Directors, EFC member, and CAMPI chair, as well as a faculty advisor of the NACE Israel Negev student section.

A. GARCIA is an industrial engineer with extensive experience in transportation systems, processes, and production equipment in turbochargers and interchange coolers. He received his diploma from the Faculty of Engineering at the Universidad Autonoma de Baja California, Mexico. He is now involved in a postgraduate study program at the Institute of Engineering to obtain a Sc. Dr. degree on corrosion performance of naval aluminum alloy in seawater.

M. SCHORR is a professor (Dr. Honoris Causa) at the Institute of Engineering, Universidad Autonoma de Baja California. He has a B.Sc. in chemistry and a M.Sc. in materials engineering from the Technion-Israel Institute of Technology, with 40 years of experience in industrial corrosion control. From 1986 to 2004, he was editor of *Corrosion Reviews*. He has published 205 scientific and technical articles on materials and corrosion in English, Spanish, and Hebrew. He has worked as a corrosion consultant and professor in Israel, the United States, Latin America, Spain, and South Africa. He has been a NACE member for 17 years. MP