CONCURRENT STUDIES OF ENHANCED HEAT TRANSFER
AND MATERIALS FOR OCEAN THERMAL EXCHANGERS

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ABSTRACT

Aluminum alloys 1100, 3003, 5052, and 6063 were examined for their compatibility with the proposed working fluids for Ocean Thermal Energy Conversion (OTEC), anhydrous ammonia, Freon 22 and propane, and mixtures of these with sea water. Such mixtures would occur if leaks develop in evaporator or condenser heat exchangers. These aluminum alloys are compatible with the anhydrous working fluids. In ammonia-sea water solutions only limited general corrosion is found in 0-30% ammonia, no corrosion in 30 - 90% ammonia, and "self limiting" pits in 90-100% ammonia so rapid deterioration of the exchangers would not occur. No corrosion was observed in sea water saturated with Freon 22 or propane. No differences in alloy performance were evident in any of these tests so selection can be made on the basis of compatibility with sea water. A review of the available literature indicates that 5052 shows the best performance in surface sea water followed by 1100, 3003 and then 6063 alloy. In deep sea water only 5052 and 1100 alloys appear suitable although more data is required. In both surface and deep sea waters, alcladding offers the best protection against tube perforation; few instances of penetration into the core alloy have been observed for the alclad alloys examined in this study.

INTRODUCTION

High costs associated with heat exchangers required for ocean thermal power plants may place a limitation on the economic feasibility of the process. Extrusions made from aluminum alloys afford the possibility of providing fluted exchanger surfaces for enhanced heat transfer at reduced materials cost over other materials of construction.

Aluminum alloys have enjoyed considerable success for structural type applications in sea water and in desalination plant heat exchangers handling both treated and untreated sea water. A review of this service experience with respect to the application of aluminum heat exchangers to Ocean Thermal Energy Conversion (OTEC) is given including performance in surface sea water characteristic of evaporator service and deep sea water characteristic of condenser service.

Aluminum alloys have been used successfully with the proposed working fluids, ammonia, Freon and propane, for many years. Their performance in anhydrous, or nearly anhydrous ammonia, is excellent as demonstrated by their application in anhydrous ammonia refrigeration systems. Aluminum and its copper free alloys have also been found to be compatible with gaseous ammonia even at temperatures to 450°C (840°F) (1) and to hot gaseous ammonia containing air (2). Aluminum alloys 1100, 3003, 5052, 6063 and 2017, which represent essentially unalloyed aluminum and Al-Mn, Al-Mg, Al-Mg-Si, and Al-Cu-Mg types, respectively, showed only mild etching after one year of exposure in liquid ammonia containing 5% H₂O at 47°C (117°F) (3).

Problems related to corrosion have developed with aluminum tubed evaporators in gas fired air conditioners employing ammonia refrigerant. To produce cooling, liquid ammonia is evaporated to form anhydrous gas leaving a small amount of residual liquid of 60% or greater ammonia remaining in the evaporator. The difficulty arises, not because of the minute amount of corrosion of the aluminum itself, but rather because of the formation of hydrogen produced by corrosion. This problem is readily solved in commercial air conditioners by trapping the hydrogen and bleeding it from the system.

In ammonia/distilled water solutions as the per cent of ammonia decreases the rate of initial corrosion increases as shown in Figure 1. For solutions of greater than 30% ammonia this initial attack is followed by passivation of the aluminum surface with little subsequent corrosion thereafter. In solutions below 30% ammonia, passivation depends on many factors - all of which relate to the buildup of a soluble aluminum species in solution required for passivation. Any factors which serve to alleviate

this buildup will prevent passivation, and excessive corrosion can occur (4). The present investigation in ammonia/sea water mixtures ranging from 0 to 100% ammonia was undertaken to determine what effects the ions in sea water would have on rates of attack and the range of stable film formation of aluminum alloys, particularly as these relate to conditions which could exist if a leak developed in a heat exchanger.

Aluminum alloys have also been widely used in refrigerating equipment handling Freons. Aluminum and its alloys are resistant to the dry gases. In the presence of moisture dissociation of the Freon can take place to form hydrochloric and hydrofluoric acids which corrode aluminum.

Aluminum is resistant to propane gas and aluminum tubing is used to handle it.

To determine the effects of these working fluids on the corrosion of aluminum for OTEC applications, tests were performed in sea water under 7.6×10^5 Pa gauge (110 psig) Freon and propane.

THE COMPATIBILITY OF ALUMINUM ALLOYS WITH SEA WATER

The use of aluminum in marine environments including atmospheric exposures, partial sea water immersion such as splash and tidal zones and total sea water immersion is well documented (5-11). For structural applications the corrosion resistant alloys maintain their integrity as measured by tensile properties for over 10 years in these environments.

In marine environments the corrosion resistant aluminum alloys corrode primarily by pitting which results in little change in cross sectional area accounting for the maintenance of properties. Even though structural integrity is important for ocean thermal heat exchangers, failure will ultimately result from perforation of the exchanger tubes so that maximum pit depth as a function of exposure time is the criteria of importance. Of secondary interest is the average depth of pit penetration, generally given as the average of the 20 deepest pits. For alloy comparisons this usually parallels but is less than the maximum pit depth. General rates of corrosion in millimeters per year (mmpy) or mils per year (mpy, thousands of an inch per year) calculated from weight loss give an indication of the total volume of metal loss, and the number of pits per unit area (pitting frequency) can be important with respect to the overall condition of the tube surface.

For the purpose of evaluating aluminum alloys for ocean thermal exchangers only those papers which included quantitative information relating to the maximum depth of attack were reviewed. Where available, average depths of attack, the calculated corrosion rate and pitting frequency are also included. The review is limited to the four exchanger alloys covered in this investigation which are considered to be representative of the corrosion resistant alloy families; 1100, essentially unalloyed aluminum, 3003, an Al-Mn alloy, 5052, an Al-Mg alloy and 6063, an Al-Mg-Si alloy. In addition, some Alclad alloys which have a metallurgically bonded 1% Zn 7072 alloy surface layer which cathodically protects the core alloy are reviewed. Comparison of these alloys will generally serve to establish the important factors affecting the corrosion performance of aluminum alloys in sea water. Numerous other alloys have been evaluated, many of which are covered in the references cited here. The reader is referred to these references for additional information.

Each of the alloys will be evaluated on the basis of its performance totally immersed in surface sea water and in the deep sea which will be a concern for this application. The effects of design factors such as crevices, galvanic couples, velocity and heavy metal ions on corrosion will also be discussed.

The Performance of Aluminum Alloys in Surface Sea Waters

Exposure studies have been conducted on aluminum alloys in surface sea water at numerous locations. Among those included in this review are exposures at Port Hueneme, Calif. (12-15), Harbor Island, N.C., Halifax, N.S., Esquimalt, B.C., Brixham, England (8), Fort Anaclor, Canal Zone (9), Key West, Florida (16), Miami, Florida, Pensacola, Florida, and Metagorda Bay, Texas (17). While some of these locations are considered to be more aggressive than others, the type of attack and relative alloy performance appears to be the same at all locations, and for the purpose of this analysis each alloy was judged on the basis of its performance at all locations.

Obtaining data from the necessarily limited size of specimens exposed in these studies serves to emphasize the random nature of pitting of aluminum alloys both with respect to pit initiation and depth of penetration. The random nature of pit initiation is illustrated by the variation in pitting frequency among specimens and in particular by the complete lack of pits on many of the panels exposed. This lack of pits on many panels exposed for longer periods also suggests that pits initiate on initial exposure; if initiation does not occur at that time, growth of the protective oxide film prevents initiation at a later time under normal exposure conditions.

nce initiation occurs propagation is rapid with pits reaching essentially their maximum depth of penetration in less than a year as shown in Figures 2-5. At some point in the life of a pit the rate of penetration decreases rapidly and/or passivation occurs. This behavior has been well documented for aluminum heat exchanger tubes in the inlet sections of a desalination materials test plant at Freeport, Texas (18, 19).

The maximum depth of penetration is variable. For example, for 1100 alloy at Esquimalt, B.C., maximum pit depths of 0.76, 0.66, and 0.38 mm (30, 26, and 15 mils) were reported for 1, 2 and 5 years, respectively, while no pits were found on the specimen exposed 10 years (Table I). For a given alloy this variation probably is related to the size and strength of local cathodes.

Examination of the data from exposure of numerous alloys suggests that another primary factor affecting depth of penetration is the alloy type or family as is illustrated by the four alloys examined here. Of the alloys evaluated 5052 alloy (Table III, Figure 4) showed the least depth of penetration followed closely by 1100 alloy (Table I, Figure 2). The critical factor in terms of ocean thermal exchanger applications is that none of the 1100 alloy specimens with exposure times up to 16 years had a pit deeper than 1.02 mm (40 mils) or for 5052 alloy with 10 years exposure deeper than 0.74 mm (29 mils). This means that for a proposed 1.27 mm (50 mils) tube wall thickness no perforations would have occurred.

Pit depths on 3003 alloy (Table II, Figure 3) would have to be considered comparable to 1100 alloy on the basis of the bulk of the data. However, there appears to be a tendency for some pits to go to greater depths prior to passivation and this factor makes it a less desirable alloy. Performance of 6063 alloy (Table IV, Figure 5) was inferior to the other alloys with pits reaching greater depths before passivation was achieved.

The results observed in this overall review appear to be consistent with the individual investigations. Goddard reported the same relative performance for 1100, 3003 and 5052 alloys as compared to the Al-Mg-Si alloys like 6063 (8). He also noted that this family of alloys is more sensitive to exposure location. This characteristic for some pits on the Al-Mg-Si alloys to continue to propagate to much greater depths was observed also by Southwell and Hummer; after 16 years exposure even though pits on 1100 and 6061 had the same average depth, the maximum pit depth on 6061 alloy was twice that on 1100 alloy. The generally better performance of 5052 alloy over 1100 and 3003 alloy is also consistent with the general observation that the Al-Mg alloys perform better in sea water applications than other alloy families.

Alclad aluminum alloys have a metallurgically bonded alloy surface which generally represents 5% of the material thickness per face clad but can be made thicker if longer cladding life is desired. The cladding alloy is selected to have an electrochemical potential negative or anodic to the core alloy and corrode preferentially protecting the core. Pits will initiate and propagate through the cladding to the core, but then corrosion proceeds laterally along the surface avoiding penetration. If properly selected, the cladding alloy will have a self-corrosion rate similar to the core so that no greater total metal loss is experienced. For most common alloys and applications 1% Zn 7072 alloy is employed for the cladding.

Table V shows the depth of penetration of pits on Alclad 3003 and 6063 alloys exposed in sea water. Even though these are not the most corrosion resistant core alloys for this application, the maximum depth of penetration in all cases did not penetrate the core after periods up to five years. Differences in maximum depth of attack in Table V are related to the different cladding thicknesses on the various panels.

Figure 6 shows a micrograph of an Alclad 3003 alloy tube exposed 10 years in the lube oil cooling system on the SS Alcoa Clipper. Sea water temperatures ranged from 24°C (75°F) to 29°C (84°F) (84°F) between the inlet and outlet. All of the tubes had a 16% cladding thickness with the exception of one which had an 8% cladding. Table VI contains a summary of performance data of the Alclad 3003 tubes for the 10 years that the unit was in operation. Only the tube which had 8% original cladding showed penetration into the core after 8 years exposure. For the tubes with 16% cladding thickness no penetration of the core alloy occurred after 10 years of service with 24% of the cladding still remaining.

Alclad 3003 alloy tubes were employed in the OSW desalination materials test plant at Freeport, Texas. As a result of the elevated temperatures, the cladding was consumed within the first six months of service (Table VII). However, no pitting of the tubes occurred with subsequent exposure as was evident on initial exposure of non-clad alloys (19). As discussed, pit initiation seems to be less likely once a thicker oxide film develops on the aluminum. The alclad in this case may have served to protect the core while this protective film was formed.

Alclad aluminum alloys offer insurance against a pit perforating the exchanger tube during the initial period of exposure and will continue to supply protection to the core alloy depending on cladding thickness for many years. In combination with the most resistant core alloy (5052 for example) many years of service life could be anticipated even after the cladding has been expended.

APPLICATION OF ALUMINUM ALLOYS IN THE DEEP SEA

Condenser water for OTEC power plants will be drawn from as deep as 457 m (1500 ft). While the exchangers themselves may not be at this depth, the sea water, with the exception of pressure, can be expected to be characteristic of the depth from which it was obtained. For example, the oxygen content at 722 m (2370 ft) is 0.40 ml/l as compared to 5.6 ml/l at the surface, the pH is 7.4 - 7.6 vs 7.87 and the salinity 34.4 vs. 33.6 parts per thousand (15).

Data has been obtained by Reinhart et al, and Ailor for depths to 2067 m (6780 ft) and up to three years exposure at Port Hueneme, Calif. (11-15), and by Wallace and Colletti at 1280 m (4200 ft) in the Tongue-of-the-Ocean, Bahamas (20). Although these results are for depths greater than anticipated for OTEC applications, the trends particularly with respect to relative alloy performance should be valid. The original references should be consulted for evaluation of additional alloys.

Table VIII gives data for 1100 alloy at various depths for periods up to three years. The maximum pit depths obtained are plotted as a function of time for the various exposure depths in Figure 7. Because the data is limited it is difficult to determine the extent to which pit propagation rates are decreasing or passivation has occurred. Generally, maximum pit depths are greater than for surface exposure although at 701 m (2300 ft) corrosion appears to be within acceptable limits.

Similar results for 3003 alloy are given in Table IX and Figure 8. These results show that performance of 3003 alloy is sensitive to depth of exposure with maximum pit depths even at 701 m (2300 ft) being excessive for OTEC applications.

The corrosion performance of 5052 alloy at various depths is given in Table X and Figure 9. The performance of this alloy appears, at least to some degree, to be related to depth, but its performance is certainly acceptable down to the 701 m (2300 ft) level with pits appearing to be self-limiting as for surface exposures. The tendency for pit growth rates for 5052 alloy to decrease with time was also noted by Ailor at the 722 m (2370 ft) exposure as contrasted to 3003 alloy where pits appeared to be growing (15).

No data is available for 6063 alloy for deep sea exposure. Results for the other alloys suggest that relative performance is similar to surface exposure and on the basis of surface exposures 6063 alloy would not appear to be as suitable a choice for deep sea applications. This is supported by comparison with the performance of 6061 alloy, also on Al-Mg-Si alloy, in deep sea exposure (12-15).

Comparing surface to deep sea exposure, Ailor has pointed out that for Mg free alloys an increase in pitting severity occurs with increasing copper content for deep sea exposures with the exception of high purity alloy 1180 which did not perform well. For Mg bearing alloys, less than 0.06% Cu is required for good corrosion performance. The overall results shown here would tend to support the superiority of Mg alloys for deep sea exposure, 1100 alloy may also be acceptable, but 3003 does not appear to be suitable. While data for 6063 alloy is not available, its performance compared to the other alloys must be questioned on the basis of surface exposure and deep sea performance of 6061 alloy.

Results for exposure of a number of specimens of Alclad 3003 alloy in deep sea water at Port Hueneme, California, indicate that with up to three years exposure penetration of the core alloy did not occur (Table XI). However, for many specimens consumption of the cladding occurred over large areas of the surface. This would indicate that either the 7072 alloy cladding, which was developed primarily for application in natural waters, is too active and undergoes high self-corrosion before it is actually required for protection of the core alloy, or the increased pitting tendency of the 3003 core may consume more of the cladding for protection. In no instance where a large per cent of the cladding was consumed did penetration into the core occur indicating that a passive film had probably been established.

Previous experience at Alcoa Laboratories indicates that two approaches can be taken to increase the longevity of a cladding in corrosive environments. To decrease the effects of self-corrosion a higher purity cladding can be employed, and if the cladding is providing more protection than actually required, the Zn content of the cladding can be reduced. In order to tailor a cladding for a specific application, however, care must be taken to ensure that the activity of the cladding is not reduced to a point where it does not supply adequate protection allowing penetration of the core.

For deep sea applications the life of the cladding may also be extended by employing a more corrosion resistant core alloy. This not only decreases the demand on the cladding but may permit the selection of an inherently more corrosion resistant cladding without loss in protection. For these alloys the cladding may supply the initial protection required while a protective oxide film is established as the core alloy is exposed.

Alclad alloys offer an approach to optimize the service life of aluminum for OTEC power plants. Selection of the core alloy should be made on the basis of maximum pit depths obtained in surface and deep sea exposures. Selection of a cladding alloy should then be made to supply adequate protection to the core while at the same time minimizing excessive consumption of the cladding.

DESIGN CONSIDERATION

Crevice Corrosion - Localized corrosion which occurs in confined spaces such as metal faying surfaces, under gaskets, scale or biofouling is termed crevice corrosion. This action may be caused by differential aeration resulting from low oxygen diffusion rates into the crevice or differential salt concentration between the bulk electrolyte and the electrolyte in the crevice. These factors cause metal in the crevice to become more anodic than the surface exposed to the bulk solution, and corrosion leads to acidification in the crevice and accelerated attack similar to the mechanisms for pitting.

In surface sea water crevice corrosion is not generally a problem with aluminum alloys. It tends to take the form of pitting and proceeds at a low rate (8). Crevice corrosion at faying surfaces (Tables I - IV) illustrate that maximum crevice depths are similar or only slightly greater than maximum pit depths. Those alloys which are most resistant to pitting (Al-Mg, 5052 alloy for example) are also most resistant to crevice corrosion. Attack under biofouling on aluminum alloy occurs as pitting and no tendency towards crevice corrosion is observed.

As with pitting crevice corrosion tends to increase with increasing ocean depths. Both 1100 and 3003 alloys displayed extensive crevice attack even at 701 m (2300 ft). Generally, 5052 alloy appeared more resistant to crevice corrosion at least at 701 m (2300 ft) although the attack is still excessive for ocean thermal applications. Alclad alloys displayed no crevice attack in excess of the cladding thickness with up to three years exposure at depths to 1615 m (5300 ft). The best protection against crevice corrosion is, of course, to design to avoid crevices or to paint faying surfaces.

Velocity Effects - In relative flow rate experiments Goddard and Booth observed that the rate of pitting decreased with increasing velocity up to some point and then increased. Similar results were observed at the Freeport desalination materials test plant (18,19). In the first plant, the first and second effects contained tubes carrying sea water at 0.8, 1.5, 3.0 m/sec (2.5, 5 and 10 ft/sec). Pitting was encountered in the tubes operating at 0.8 m/sec (2.5 ft/sec). During the last year of operation the velocity was increased from 0.8 to 1.5 m/sec. (2.5 to 5.0 ft/sec) in these exchangers, and pitting was eliminated, indicating that increased velocities did reduce pitting.

Galvanic Corrosion - Because of its anodic potential, galvanic attack of aluminum alloys will occur if they are coupled to most other metals in sea water, including copper and copper alloys and steels or stainless steels. All aluminum construction or the use of aluminum with non-metals is preferred. At the desalination materials test center the problem of galvanic corrosion of aluminum piping coupled to stainless steel cast alloy 20 pumps was reduced to a practical level under deaerated conditions by placing 152 mm (6") plastic lined pipe inserts between the steel and aluminum (18). In a desalination plant operated for OSW by Reynolds Metals Co., the problem was resolved by placing "doughnut-shaped" anodes between pipe and pump flanges. These anodes corroded to protect the aluminum and were simple to install and maintain (23).

Heavy Metal Ions - Again, because they are anodic, aluminum alloys will tend to scavenge heavy metals such as copper, nickel, tin, lead and mercury if they are present at greater than several parts per billion in sea water. Once these metals plate onto the surface small galvanic cells are created which lead to pitting of the surface. Mercury can be particularly troublesome because of its tendency to amalgamate with the aluminum preventing protective film formation. For most OTEC applications which are removed from industrial coastlines, and which will not employ copper alloys upstream of the aluminum, the presence of these ions should not be a problem. It has been shown in desalination plant applications, that heavy metal plating can be decreased by preconditioning the tubes with boiling deionized water to build up the protective oxide prior to sea water exposure (18). Alclad alloys are also recommended where heavy metal scavenging is considered a possibility.

EXPERIMENTAL

Ammonia/Sea Water Tests

To determine the effect of leakage on the corrosion performance of aluminum alloys, tests were run in ammonia/sea water solutions ranging from 0 to 100% ammonia. Solutions of 28% and less were prepared from reagent grade ammonium hydroxide. The concentration of the stock solution was determined by adding standard HCl solution in excess and back titrating with 1 N NaOH.

Solutions containing more than 30% ammonia were prepared from USS premium grade anhydrous ammonia (99.999%) and deionized water. The ammonia was distilled from the cylinder, as illustrated in Figure 10, condensed in a coiled aluminum tube submerged in a dry ice isopropanol bath, and collected in a stainless

steel holding vessel also in a dry ice isopropanol bath. The distillation system was purged with N_2 prior to collection to eliminate moisture.

On the basis of the estimated flow rate, an appropriate weight of ammonia was collected, and then the holding tank sealed and warmed to room temperature. After weighing the vessel, ammonia was released until the required weight (within ± 0.5 gm) of ammonia was obtained.

While these operations were being performed the required weight of water was placed in a glass beaker with 33.6 gms of Lake Products synthetic sea salt (Table XII) to give a concentration equivalent to 1X sea salt in the final 800 ml volume of solution. The weight of water and ammonia were selected to give the desired solution composition in a total volume of 800 ml. The weight per cent compositions in this paper refer only to the ratio of ammonia to water and do not account for the weight of salt added.

Once the sea salt was dissolved, the beaker was placed in the pressure vessel and the lid sealed. The ammonia holding tank was then coupled to the vessel (Figure 11), and while stirring the sea water solution rapidly with a magnetic stirring bar, the ammonia was added. On addition of the ammonia, large quantities of salt precipitated from solution; no attempt has been made to identify the concentrations of various salts left in solution for the various ammonia-water concentrations.

Specimens were sheared from 1100-H18, 3003-H18, 5052-H34, and 6063-T5 alloys with the nominal compositions given in Table XIII. For the corrosion versus time experiments the specimens were 10.1 cm x 1.3 cm x 0.163 cm (4 in. x 0.5 in. x 0.064 in.) thick sheet except for the 6063 alloy specimens which were cut from a 0.241 cm (0.09 in.) thick extrusion. The specimen surface area was 29.5 cm² (4.6 in²) which gave a specimen area to solution volume ratio (A/V) of 0.037 cm⁻¹. To determine the effects of area to volume ratio on corrosion in dilute solutions various size specimens were also run as indicated in Table XIV.

Each specimen was prepared by degreasing with acetone and immersing it in an aluminum cleaning solution (60 gms CrO_3 , 105 ml H_3PO_4 and 2,763 ml D.I. water) for 5 minutes at 85°C (185°F) to remove surface films which might increase the initiation time for corrosion. The specimens were rinsed in D.I. water, air dried and weighed to ± 0.1 mg. After exposure the specimens were again cleaned with the above solution, reweighed and their corrosion performance evaluated on the basis of weight loss.

With the exception of the larger specimens in the area/volume experiments which had to be exposed at an angle, all of the specimens were exposed hanging vertically as indicated in Figure 11. In dilute solutions the various alloys were exposed independently and together in the same beaker. On the basis of those results tests in concentrated solutions were generally run with all specimens exposed together.

Velocity Tests - To evaluate the effect of velocity on corrosion 30.5 cm (12 in.) tube specimens of 3003 alloy were exposed to 5% ammonia-95% sea water solution at velocities of 1.2 m (4 ft) and 2.4 (8 ft) per second. Besides the specimens 3003 alloy tubing was also employed for the rest of the flow loop (Figure 12) as well as a cooling coil used to maintain a constant temperature. Considering the total surface area of aluminum exposed to the volume of solution, an area to volume ratio of 0.06 cm^{-1} existed.

Prior to testing, each specimen was acetone degreased and weighed, and after the test which ran 14 days, each specimen was cleaned in chromic acid-phosphoric acid solution and reweighed to establish the corrosion rate. Polyvinyl tubing was used to connect the specimen to the system. This isolated the specimen from the system and provided a quick method for assembly and disassembly without damaging the specimen.

The solution was pumped with a stainless steel pump. To establish a velocity of 1.2 m/sec. (4 ft/sec) solution was pumped at 7.75 liters/min. through 1.1 cm (0.4 in.) diameter tubing. Because of limited pump capacity, a volume of 6.5 liter/min. was pumped through .7 mm (0.3 in.) tubing to obtain 2.4 m/sec. (8 ft/sec) velocity.

Galvanic Corrosion - Galvanic corrosion tests were run in anhydrous ammonia and nearly anhydrous ammonia to determine the compatibility of aluminum with steel and stainless steel components, for example, pumps which might be employed in the working fluid system. Each aluminum specimen was a 5.1 cm x 10.2 cm x 0.163 cm (2 in. x 4 in. x 0.064 in.) thick 1100 alloy flag. Similarly, flags of 5.1 cm x 10.2 cm x 0.20 cm (2 in. x 4 in. x 0.08 in.) thick mild steel and 316 stainless steel and 5.1 cm x 10.2 cm x 1.27 cm (2 in. x 4 in. x 0.5 in.) T-1 steel were employed. Aluminum specimens were cleaned with concentrated nitric acid (70%) to remove any iron embedded during preparation. Each aluminum or steel specimen was mounted to a conax conductor gland and spaced approximately 0.16 cm (0.063 in.) apart. Electrical contact was made externally and the current monitored with a Hewlett Packard micro-volt ammeter. Tests were run in both aerated and deaerated solutions.

FREON/SEA WATER AND PROPANE/SEA WATER TESTS

Corrosion caused by Freon or propane leakage into the sea water side of the heat exchangers was evaluated by placing aluminum alloy specimens in 1X sea water with 7.6×10^5 Pa gauge (110 psig) gas maintained above the solution. Corrosion rates were determined by weight loss as described previously.

RESULTS AND DISCUSSION

Ammonia/Sea Water Tests

Figures 13-20 give the weight loss versus time curves obtained in this study. Scatter in the data, particularly in the more dilute solutions, is typical of previous experience in ammonia/water solutions and relates to the initial condition of the aluminum surface which subtly affect the rate of initial attack and more importantly the time required for the second stage of decreased corrosion to be reached.

In 5%, 10% and 30% solutions, the different alloys were exposed individually and with all of the specimens in the same beaker. As can be seen, weight losses on specimens exposed individually were somewhat greater than for those exposed together, but this difference was considered insignificant particularly with respect to the effect on the final corrosion rate (final slope of the curve), and so specimens were exposed together only in the more concentrated solutions requiring pressure vessels. No significant differences among the alloys was observed.

Attack in 5% and 10% ammonia was general in nature. Table XV gives both the initial corrosion rates and final corrosion rates of the alloys in 5% and 10% ammonia calculated from the weight loss in the first week of exposure and the final slope of the weight loss time curve, respectively. Based on the final corrosion rate, attack in these solutions can be considered insignificant. The initial corrosion rates give an indication of the highest rate of attack that can be achieved if for some reason conditions are not met (for example, film formation) for the final corrosion rate to be realized. Even in these circumstances corrosion is not catastrophic.

Related data obtained by Alcoa for ammoniated brine cooler applications is similar to that obtained in this study. Panels of 3003-H14, Alc. 3003-H14, 5052-H34, 6061-T6 and 6063-T6 alloys exposed to a brine solution containing 26% NaCl, 8.1% NH_3 and 4.9% CO_2 with traces of sulfide in a preliminary ammonia absorber showed only slight etching and minute pitting 0.02 mmpy (0.6 mpy) after 78 days. Similarly, aluminum tubes inspected after 2 years service in an ammoniated brine cooler (3% NaCl, 9% NH_3 and 0.1% H_2S) showed no significant attack.

In 30% to 70% ammonia the attack on all of the alloys is only mild etching appearing to remain uniform for the duration of the test. Rates of attack were insignificant.

In 90% to 100% ammonia attack of the aluminum alloys was by pitting as shown for 1100 alloy in Figure 21. Initial rates of attack increase with concentration in this range. In 90% and 95% ammonia the rates of attack appear to remain essentially constant with time but visual examination revealed that the weight loss after the first week is at least in part a result of the attack spreading laterally rather than the pits becoming deeper. This is verified by metallographic examination which show no increase in average or maximum depth of attack after the first week of exposure (Table XVI).

In 100% ammonia the weight loss time curve indicates essentially no further significant attack after the first week of exposure, and this is evidenced by the surface photographs for 1100 and 6063 alloy in Figure 21A and B. Again, depths of penetration also did not increase after the first week of exposure (Table XV). In 100% ammonia 1100 and 6063 alloys had the least depth of attack followed by 5052 and 3003 alloy although the differences do not appear significant.

Figure 22 summarizes the one month exposure data for 1100, 3003, 5052 and 6063 alloys (exposed together) as a function of solution concentration. Comparison of these curves emphasizes the similarity among the alloys in ammonia/sea water solution. In all cases maximum attack occurred in the 5% to 10% ammonia concentration range.

One of the factors which was previously identified as significant for the passivation of aluminum alloys in dilute ammonia/water solutions was the effect of the ratio of specimen area to solution volume. As shown in Figure 23, the smaller the exposed specimen area or A/V the greater the weight loss per unit area. Comparison with Figure 24 for 1100 alloy in ammonia/sea water solutions show that the presence of sea salts in dilute solution not only reduces the amount of attack but also reduces the effect of A/V to an insignificant level. No effect of A/V was observed in 30% ammonia (Figure 25). With the exception of the smallest specimens which show an anomalous behavior the weight loss per unit area in 5% and 10% ammonia decreases with increasing A/V but the overall change is only 1 mg/cm^2 .

Velocity Effects

Figure 26 shows the appearance of specimens exposed 14 days in 5% ammonia at 1.2 m (4 ft) and 2.4 m (8 ft) per second at an area to volume ratio of 0.06 cm^{-1} . This ammonia concentration was selected because it is the most aggressive. The weight losses under these conditions were 1.72 gm/cm^2 and 0.60 mg/cm^2 , respectively. This compares with about 2.5 gm/cm^2 for an A/V ratio of 0.06 cm^{-1} in quiescent solution (Figure 25). Attack was uniform in nature with no pitting. This decrease in weight loss with increasing solution velocity was observed in more concentrated ammonia/water solutions previously (4). This may be a result of the increase in the diffusion rate of OH^- ions to the aluminum surface so that the solution behaves as if it were slightly more concentrated and passivation occurs more readily.

Galvanic Corrosion

Figure 27 gives galvanic corrosion currents for 1100 and 3003 alloys coupled to T-1, 316SS and mild steel in air contaminated ammonia. Round bottom pitting attack occurs on the aluminum as shown in Figure 28 for 1100 alloy coupled to 316SS. Aluminum alloys should not be coupled to steels in anhydrous ammonia under these conditions. Figure 29 shows that as the moisture content of the ammonia is increased in aerated ammonia, the rate of galvanic attack decreases. (24)

Currents developed for 1100 alloy coupled to mild steel and 316SS in deaerated ammonia are shown in Figure 30. After an initial current spike, probably as a result of the reduction of adsorbed oxygen on the steel, the current decreases to zero. Pitting corrosion is evident on these specimens, but at a much lower level than in aerated solutions, and the galvanic current curves suggest that they greatly decreased to very low rates after the first couple of days of exposure.

Freon/Sea Water and Propane/Sea Water Tests

Figures 31 and 32 show the weight loss of 1100, 3003, 5052 and 6063 alloys exposed in sea water under $7.6 \times 10^{-5} \text{ Pa}$ (110 psig) pressure of Freon 22 and propane, respectively. No corrosion above that experienced in sea water alone was observed.

CONCLUSIONS

The aluminum alloys examined in this investigation, 1100, 3003, 5052 and 6063 are compatible with the proposed OTEC working fluids, anhydrous ammonia, Freon 22, and propane. Tests of these alloys with 0-100% ammonia-sea water solutions indicate that general corrosion occurs in dilute (0-30% ammonia) solutions and "self limiting" pitting can occur in concentrated (90-100% ammonia) solutions. Even under flow conditions, however, rapid deterioration of aluminum heat exchangers will not occur should a leak develop. Similarly, no significant corrosion of these alloys was observed in sea water saturated with Freon 22 or propane. No differences were observed among the alloys in these tests so alloy selection can be made on the basis of compatibility with sea water.

Analysis of the available literature on the corrosion of these aluminum alloys in surface sea water shows that the depths of pit penetration on these four alloys are "self limiting" reaching their maximum depth of penetration on initial exposure followed by complete passivation or limited growth thereafter. The least depth of penetration was found on the Al-Mg alloy 5052 illustrating the generally better sea water corrosion performance of this alloy family. Both 1100 alloy, essentially unalloyed aluminum, and 3003 alloy, and Al-Mn alloy, also showed acceptable behavior. Performance of 6063, an Al-Mg, Si alloy, was slightly inferior with maximum pit depths sometimes exceeding 1.27 mm (0.050 inch) the anticipated wall thickness for exchanger tubes.

Alclad aluminum alloys which have a metallurgically bonded anodic layer to galvanically protect the core alloy are the best choice for exchangers in surface sea water. Penetration occurs only to the core and then proceeds laterally; in very few cases has penetration into the core been observed.

Alloy corrosion performance in deep sea water parallels that in surface sea water except depths of attack are greater. The limited data available makes it difficult to ascertain whether pit penetration ceases with time. Only 5052 and 1100 alloys appear to offer possibly acceptable performance for the single alloy materials. Although the cladding on Alclad alloys is in many instances almost entirely consumed, in no case has attack penetrated into the core indicating that protection may be adequate to allow protective film formation on the core alloy to occur. The use of alcladding with the most corrosion resistant core alloy appears to be the best approach for OTEC heat exchangers for deep sea exposures.

RECOMMENDATIONS

These results indicate that a need exists to develop an alclad aluminum alloy especially for deep sea exposures. Rapid consumption of the 1% Zn 7072 cladding alloy, which was developed for natural waters, indicates that either the cladding is too active having too high of a self-corrosion rate or the increased tendency of the core alloys tested towards pitting in the deep sea consumes the cladding too rapidly.

A high self corrosion rate of the cladding can be overcome by decreasing the activity of the cladding through decreased Zn content and/or increased purity of the alloy. Demand on the cladding can be reduced by selecting a more corrosion resistant core alloy, 5052, for example. These modifications in cladding-core combinations must be made with care to ensure that adequate protection is still provided by the cladding.

By extending the cladding life and with the indication that the cladding allows the core alloy once exposed to develop a protective oxide, long service life could reasonably be assured with the use of a properly clad corrosion resistant alloy.

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TABLE I

PERFORMANCE OF 1100 ALLOY IN SURFACE SEA WATER

Alloy	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Crevice Depth		Location	Ref.
		(mmpy)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
1100-H14	0.5	0.036	1.4	0.00	0	---	---	0.13	5	Port Hueneme, Calif.	(12-14)
	1	0.015	0.6	0.33	13	---	---	0.33	13		
1100-H14	1	0.008	0.33	0.00	00	---	---	---	---	Harbor Island, N.C.	(8)
	2	0.005	0.20	0.00	0	---	---	---	---		
	5	0.004	0.15	1.02	40	---	---	---	---		
	10	0.002	0.08	0.00	0	---	---	---	---		
1100-H14	1	0.004	0.14	0.43	17	---	---	---	---	Halifax, N.S.	(8)
	2	0.003	0.13	0.81	32	---	---	---	---		
	5	0.002	0.08	0.00	0	---	---	---	---		
	10	0.003	0.10	0.74	29	---	---	---	---		
1100-H14	1	0.000	0.00	0.76	30	---	---	---	---	Esquimalt, B.C.	(8)
	2	0.002	0.09	0.66	26	---	---	---	---		
	5	0.001	0.02	0.38	15	---	---	---	---		
	10	0.001	0.02	0.00	0	---	---	---	---		
1100	0.5	---	---	0.02	0.6	---	---	---	---	Brixham, England	(8)
	2.6	---	---	0.10	4	---	---	---	---		
	5	---	---	0.33	13	---	---	---	---		
	10	---	---	0.28	11	---	---	---	---		
1100	1	0.007	0.28	0.38	15	0.23	9	---	---	Fort Amador, Canal Zone	(9)
	2	0.005	0.20	0.20	8	0.08	3	---	---		
	4	0.004	0.16	0.38	15	0.18	7	---	---		
	8	0.002	0.08	0.48	19	0.28	11	---	---		
	16	0.003	0.10	0.84	33	---	---	---	---		
1100-H14	1	---	---	0.03	1	---	---	0.10	4	Key West, Fla.	(16)
1100-F	1	---	---	0.03	1	---	---	0.31	12		

TABLE II
PERFORMANCE OF 3003 ALLOY IN SURFACE SEA WATER

Alloy	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Crevice Depth		Location	Ref.
		(mmpy)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
3003-H14	0.5	0.028	1.1	0.84	33	0.46	18.1	0.0	0	Port Hueneme, Calif.	(12-14)
3003	0.5	0.025	1.0	I(1)	I	---	---	0.0	0		
3003	1	0.015	0.6(2)	I(1)	I	---	---	0.0	0		
3003-H14	1	0.025	1.0(2)	0.53	21	0.37	14.6	0.0	0		
3003-H14	1.5	0.008	0.3(2)	0.86	34	0.86	34	1.91	75		
3003-H14	1.5	0.051	2.0(2)	1.65	65	1.25	49	0.0	0		
3003-H14	1	0.008	0.31	0.00	0	---	---	---	---	Harbor Island, N.C.	(8)
	2	0.006	0.24	0.00	0	---	---	---	---		
	5	0.004	0.14	0.33	13	---	---	---	---		
	10	0.002	0.08	0.53	21	---	---	---	---		
3003-H14	1	0.000	0.00	0.33	13	---	---	---	---	Halifax, N. S.	(8)
	2	0.003	0.12	0.38	15	---	---	---	---		
	5	0.002	0.07	0.53	21	---	---	---	---		
	10	0.002	0.06	0.56	22	---	---	---	---		
3003-H14	1	0.000	0.00	0.13	5	---	---	---	---	Esquimalt, B. C.	(8)
	2	0.000	0.00	0.51	20	---	---	---	---		
	5	0.001	0.05	0.00	0	---	---	---	---		
	10	0.001	0.02	0.25	10	---	---	---	---		
3003	0.5	---	---	0.02	0.7	---	---	---	---	Brixham, England	(8)
	5	---	---	0.13	5	---	---	---	---		
	10	---	---	1.17	46	---	---	---	---		
3003-H14	1	---	---	0.81	32	0.46	18	0.31	12	Key West, Fla.	(16)
3003-F	3	---	---	0.15	5.8	---	---	---	---	Matagorda Bay, Tx.	(17)
	3	---	---	0.11	4.3	---	---	---	---		
	6	---	---	0.18	7.1	---	---	0.85	33.3		
3003-H14	8.3	---	---	0.11	4.2	0.05	1.8(2)	---	---	Pensacola, Fla.	(17)
3003-H14	2	0.013	0.5	0.43	16.8	0.14	5.6	---	---	Corpus Christi, Tx.	(17)

(1) Incipient.
(2) Exfoliation

TABLE III
PERFORMANCE OF 5052 ALLOY IN SURFACE SEA WATER

Alloy	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Crevice Depth		Location	Ref.
		(mm/yr)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
5052-0	.5	0.030	1.2	I(1)	I	---	---	0.0	0	Port Hueneme, Calif.	(12-14)
	1	0.015	0.6	0.13	5.0	---	---	0.13	5		
5052-H34	1	0.009	0.34	0.00	0	---	---	---	---	Hambor Island, N.C.	(8)
	2	0.006	0.24	0.00	0	---	---	---	---		
	5	0.004	0.14	0.00	0	---	---	---	---		
	10	0.003	0.11	0.00	0	---	---	---	---		
5052-H34	1	0.005	0.21	0.13	5	---	---	---	---	Halifax, N.S.	(8)
	2	0.003	0.12	0.51	20	---	---	---	---		
	5	---	---	0.15	6	---	---	---	---		
	10	0.003	0.11	0.31	12	---	---	---	---		
5052-H34	1	0.003	0.12	0.41	16	---	---	---	---	Esquimalt, B.C.	(8)
	2	0.000	0.00	0.15	6	---	---	---	---		
	5	0.000	0.00	0.0	0	---	---	---	---		
	10	0.000	0.00	0.13	5	---	---	---	---		
5052	1	0.007	0.29	0.08	3	---	---	---	---	Freeport, Tx.	(8)
5052	2	0.003	0.11	0.00	0	---	---	---	---	Cape Beale, B.C.	(8)
5052	1	0.003	0.11	0.00	0	---	---	---	---	Galiano	(8)
5052	.5	---	---	0.01	0.3	---	---	---	---	Brixham, England	(8)
	5	---	---	0.43	17	---	---	---	---		
5052-H32	1	---	---	0.03	1	---	---	0.10	4	Key West, Fla.	(16)
5052-H34	8.3	---	---	0.04	1.4	0.02	0.6	---	---	Pensacola, Fla.	(17)
5052-H34	2	0.023	0.9	0.36	14	0.14	5.6	---	---	Corpus Christi, Tx.	(17)

(1) Incipient

Continued

Table III (Continued)

Alloy	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Crevice Depth		Location	Ref.
		(mmpy)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
5052-H34	1	---	---	0.74	29.0	0.30	11.6	---	---	Miami, Fla.	(17)
5052	1	---	---	0.37	14.5	0.17	6.5	---	---		
5052	1	---	---	0.07	2.9	0.02	0.9	---	---		
5052-0	2	---	---	0.03	1.3	0.02	0.7	---	---		
5052-0	2	---	---	0.06	2.5	0.04	1.2	---	---		
5052-0	3	---	---	0.03	1.2	0.02	0.8	---	---		
5052-0	3	---	---	0.09	3.4	0.02	0.9	---	---		
5052-0	5	---	---	0.04	1.4	0.02	0.8	---	---		
5052-0	5	---	---	0.21	8.4	0.04	1.2	---	---		

TABLE IV

PERFORMANCE OF 6063 ALLOY IN SURFACE SEA WATER

Alloy	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Crevice Depth		Location	Ref.
		(mm/yr)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
6063-T5	1	0.006	0.22	1.07	42	---	---	---	---	Harbor Island, N.C.	(8)
	2	0.004	0.14	0.89	35	---	---	---	---		
	5	0.003	0.11	1.14	45	---	---	---	---		
6063-T5	1	0.005	0.21	0.69	27	---	---	---	---	Halifax, N.S.	(8)
	2	0.004	0.15	0.64	25	---	---	---	---		
	5	0.002	0.08	0.76	30	---	---	---	---		
6063-T5	1	0.014	0.56	1.78	70	---	---	---	---	Esquimalt, B.C.	(8)
	2	0.014	0.57	1.68	66	---	---	---	---		
	5	0.006	0.22	3.45	136	---	---	---	---		
6063-T832	1	----	----	0.55	21.7	---	---	---	---	Miami, Fla.	(17)
-T6	1	----	----	0.82	32.3	---	---	---	---		
-T4	1	---	---	0.84	32.9	---	---	---	---		
-T5	1	----	----	0.34	13.5	0.15	5.8	---	---		
-T5	1	----	----	0.55	21.5	0.23	9.0	---	---		
-T5	1	----	----	0.53	20.8	0.17	6.8	---	---		
-T6	1	----	----	0.54	21.1	0.17	6.8	---	---		
-T5	2	----	----	0.53	20.9	0.26	10.4	---	---		
-T5	2	----	----	0.45	17.8	0.23	9.0	---	---		
-T5	2	----	----	0.36	14.0	0.17	6.8	---	---		
-T6	2	----	----	0.33	13.0	0.17	6.8	---	---		
-T6	2	----	----	0.29	11.5	----	---	---	---		
-T6	2	----	----	0.52	20.5	----	---	---	---		
6063-T6	3	---	---	0.42	16.5	---	---	---	---		
6063-T6	3	---	---	0.55	21.5	---	---	---	---		

Continued

Table IV (Continued)

Alloy	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Crevice Depth		Location	Ref.
		(mmpy)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
6063-T5	3	---	---	0.30	11.6	0.04	1.5	---	---	Matagorda Bay, Tx.	(17)
-T6	3	---	---	0.11	4.3	---	---	---	---		
-T5	5	---	---	1.84	72.3	---	---	2.97	117		
-T6	6	---	---	0.15	5.8	---	---	0.20	8		

TABLE V

PERFORMANCE OF ALCLAD ALLOYS IN SURFACE
SEA WATER

Alloy	Time (Yrs)	Rate		Max. Pit Depth		Cladding Thickness		Avg. Pit Depth		Crevice Depth		Cladding Thickness		Location	Ref.
		(mm/yr)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
Alc. 3003-H12	0.5	0.025	1.0	I(1)	I	----	----	----	----	0.00	0	----	----	Port Hueneme, Calif.	(12-14)
Alc. 3003	0.5	0.025	1.0	0.05	2	----	----	----	----	0.00	0	----	----		
Alc. 3003	1	0.013	0.5	0.05	2	----	----	----	----	0.00	0	----	----		
Alc. 3003-H12	1	0.028	1.1	0.41	16	----	----	0.39	15.3	0.00	0	----	----		
Alc. 3003-H12	1.5	0.008	0.3	0.41	16	----	----	0.22	8.6	0.00	0	----	----		
Alc. 3003-H12	1.5	0.046	1.8	0.43	17	----	----	0.39	15.5	0.00	0	----	----		
Alc. 3003	1	0.008	0.32	0.00	0	----	----	----	----	----	----	----	----	Harbor Island, N.C.	(8)
	2	0.011	0.45	0.31	12	----	----	----	----	----	----	----	----		
Alc. 3003	1	0.003	0.12	0.00	0	----	----	----	----	----	----	----	----	Halifax, N. S.	(8)
	2	0.002	0.09	0.33	13	----	----	----	----	----	----	----	----		
Alc. 3003	2	0.004	0.14	0.33	13	----	----	----	----	----	----	----	----	Esquimalt, B.C.	(8)
Alc. 3003-H14	0.5	----	----	0.06	2.5	0.14	5.5	0.04	1.5	----	----	----	----	Los Angeles Harbor, Calif.	(17)
Alc. 3003-H14	0.5	----	----	0.04	1.6	0.10	4.1	0.02	0.7	----	----	----	----		
Alc. 3003-H14	0.5	----	----	0.03	1.2	0.04	1.5	0.01	0.4	----	----	----	----		
Alc. 3003-H14	2	----	----	0.06	2.5	0.15	5.8	0.02	0.6	----	----	----	----		
Alc. 3003-H14	2	----	----	0.07	2.8	0.15	5.8	0.02	0.7	----	----	----	----		
Alc. 3003-H14	2	----	----	0.04	1.4	0.04	1.5	0.03	1.1	----	----	----	----		
Alc. 3003-H14	3	----	----	0.02	0.7	----	----	0.01	0.4	----	----	----	----		
Alc. 3003-H14	3	----	----	0.06	2.3	----	----	0.05	1.8	----	----	----	----		
Alc. 3003-H14	5.4	----	----	0.09	3.6	0.10	4.1	0.06	2.5	----	----	----	----		
Alc. 3003-H14	5.4	----	----	0.06	2.4	0.10	4.1	0.05	1.9	----	----	----	----		
Alc. 3003-H14	1	----	----	0.07	2.7	0.14	5.6	0.04	1.5	----	----	----	----	Redande Beach, Calif.	(17)
Alc. 3003	8	----	----	0.06	2.5	----	----	----	----	----	----	----	----	Daytona Beach, Fla.	(6)
Alc. 6063-T5	3	----	----	0.17	6.6	----	----	----	----	----	----	----	----	Matagorda Bay, Tx.	(17)
Alc. 6063-T5	6	----	----	0.14	5.6	0.13	5.3	----	----	0.14	5.3	0.15	5.6		
Alc. 6063-T6	6	----	----	0.57	22.4	1.15	45.2	----	----	----	----	----	----		
Alc. 6063-T6	6	----	----	0.10	4.1	0.10	4.1	----	----	0.11	4.5	0.11	4.5		

(1) Incipient

TABLE VI

SS ALCOA CLIPPER ALCLAD 3003 HEAT EXCHANGER
TUBES

<u>Years of Exposure</u>	<u>% Cladding Consumed (1)</u>	<u>Maximum Remaining Cladding Thickness</u>		<u>Maximum Core Penetration</u>
		<u>(mm)</u>	<u>(mils)</u>	
1 Year	----	0.25	10.0	None detected
1 Year	5%	----	----	None detected
2.7 Years	10%	----	----	None detected
4 Years	----	0.25	10.0	None detected
4 Years	----	0.18	7.0	None detected
5 Years	50%	0.13	5.1	None detected
7 Years	53%	0.27	10.7	None detected
8 Years	90% (2)	0.13	5.0	0.52 mm (22 mils)
9 Years	50%	0.26	10.3	None detected
10 Years	76%	0.26	10.2	None detected

(1) 16% cladding except where noted

(2) 8% cladding

TABLE VII

EVALUATION OF TUBES FROM THE HEAT REJECT EXCHANGER, FREEPORT, TEXAS (18,19)

Alloy	Time (Mo.)	Max. Pit Depth		Avg. Pit Depth		Pits/cm ²
		(mm)	(mils)	(mm)	(mils)	
<u>Treated Sea Water (1)</u>						
Alc. 3003	13	0.00	0	0.00	0(2)	0
	26	0.00	0	0.00	0	0
3003	13	<0.01	<0.5	----	----	0.2
	26	0.13	5	0.03	1	<0.2
5052	13	0.38	15	0.18	7	0.2
	26	0.38	15	0.13	5	<0.2
6063	13	0.18	7	0.13	5	<0.2
	26	0.25	10	0.13	5	0.5
<u>Raw Sea Water</u>						
3003	6	0.00	0	0.00	0	0
	6(3)	0.00	0	0.00	0	<0.002
	12	0.00	0	0.00	0	0
5052	6	0.20	8	0.05	2	0.2
	6(3)	1.25	49(4)	0.76	30	0.002
	12	0.51	20	----	----	----
6063	6	0.03	1	0.00	0	0
	6(3)	1.25	49(4)	0.76	30	0.002
	12	0.00	0	0.00	0	0

(1) pH 6.5 - 7, deaerated

(2) Depth of penetration into core cladding entirely removed

(3) Second 6 mo. period of exposure

(4) Perforation

TABLE VIII

PERFORMANCE OF 1100 ALLOY IN DEEP SEA WATER

Alloy	Depth (m)	Time (Yr.)	Rate		Max. pit Depth		Avg. Pit Depth		Crevice Depth		Location	Reference
			(mmpy)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
1100-H14	713 (2340 ft.)	.5	0.142	5.6	0.00	0	----	----	1.58	62 (PR)	Port Hueneme, Calif.	(12-14)
1100-H14	713 (2340 ft.)	.5	<0.003	<0.1	0.58	23	----	----	0.0	0		
1100-H14	713 (2340 ft.)	1	0.041	1.6	0.00	0	----	----	1.58	62 (PR)		
1100-H14	722 (2370 ft.)	1	0.023	0.9	I	I (1)	----	----	1.27	50 (PR)		
1100-F	1280 (4200 ft.)	1	----	----	0.76	30	0.76	30	----	----	Tongue-of-the-Ocean, Bahamas	(20)
1100-F	1280 (4200 ft.)	1	----	----	1.52	60	0.76	30	----	----		
1100-F	1280 (4200 ft.)	1	----	----	0.51	20	0.51	20	----	----		
1100-F	1280 (4200 ft.)	1	----	----	0.00	0	0.00	0	----	----		
1100-H14	1615 (5300 ft.)	3	0.076	3.0	0.00	0	----	----	1.58	62 (PR)	Port Hueneme, Calif.	(12-14)
1100-H14	1719 (5640 ft.)	.3	0.051	2.0	0.99	39	----	----	0.0	0		
1100-H14	1719 (5640 ft.)	2	0.114	4.5	0.00	0	----	----	1.58	62 (PR)		
1100-H14	2067 (6780 ft.)	1	0.107	4.2	0.00	0	----	----	1.58	62 (PR)		

(1) Incipient

TABLE IX

PERFORMANCE OF 3003 ALLOY IN DEEP SEA WATER

Alloy	Depth (m)	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Freq. (Pits/ cm ²)	Crevice Depth		Location	Reference
			(mmpy)	(mpy)	(mm)	(mils)	(mm)	(mils)		(mm)	(mils)		
3003-H14	713 (2340 ft.)	.5	0.061	2.4	1.22	48.0	0.41	16.0	0.25	0.71	28	Port Hueneme, Calif.	(12-14)
3003	713 (2340 ft.)	.5	0.036	1.4	0.00	0	----	----	----	1.02	40 (PR)		
3003-H14	713 (2340 ft.)	.5	<0.003	<0.1	0.43	17	----	----	----	0.0	0		
3003-H14	722 (2370 ft.)	1	0.036	1.4	2.31	91.0	----	----	----	1.02	40 (PR)		
3003	722 (2370 ft.)	1	0.028	1.1	0.00	0	----	----	----	1.02	40		
3003-H14	722 (2370 ft.)	1	0.021	0.84	1.07	42.0	0.37	14.5	----	----	----	Port Hueneme, Calif.	(15)
3003-F	1280 (4200 ft.)	1	----	----	0.51	20	0.51	20	----	----	----	Tongue-of-the- Ocean, Bahamas	(20)
3003-F	1280 (4200 ft.)	1	----	----	1.27	50	1.27	50	----	----	----		
3003-F	1280 (4200 ft.)	1	----	----	0.51	20	0.51	20	----	----	----		
3003-F	1280 (4200 ft.)	1	----	----	1.52	60	0.76	30	----	----	----		
3003-H14	1615 (5300 ft.)	3	0.053	2.1	0.74	29	0.31	12.1	0.08	3.18	125 (PR)	Port Hueneme, Calif.	(12-14)
3003-H14	1615 (5300 ft.)	3	0.056	2.2	3.18	125 (PR)	2.16	85	0.22	2.34	94		
3003	1615 (5300 ft.)	3	0.071	2.8	----	----	----	----	----	----	----		
3003-H14	1719 (5640 ft.)	.3	0.013	0.5	0.69	27	0.49	19.4	0.74	0.81	32		
3003	1719 (5640 ft.)	.3	0.015	0.6	0.000	0	----	----	----	0.71	28		
3003-H14	1719 (5640 ft.)	2	0.058	2.3	3.18	125 (PR)	1.63	64.1	0.2	3.18	125 (PR)		
3003	1719 (5640 ft.)	2	0.076	3.0	0.000	0	----	----	----	1.02	40 (PR)		
3003-H14	2067 (6780 ft.)	1	0.099	3.9	3.18	125 (PR)	2.09	82.2	0.06	1.68	66		
3003	2067 (6780 ft.)	1	0.097	3.8	0.00	0	----	----	----	1.27	50 (PR)		

TABLE X

PERFORMANCE OF 5052 ALLOY IN DEEP SEA WATER

Alloy	Depth (m)	Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Crevice Depth		Location	Ref.
			(mmpy)	(mpy)	(mm)	(mils)	(mm)	(mils)	(mm)	(mils)		
5052-0	713 (2340 ft.)	.5	0.046	1.8	0.0	0	----	----	1.65	65 (PR)	Port Hueneme, Calif.	(12-14)
5052-H32	713 (2340 ft.)	.5	----	----	Uniform	Uniform	----	----	0.00	0		
5052-H34	713 (2340 ft.)	.5	<0.003	<0.1	0.31	12	----	----	0.00	0	Port Hueneme, Calif.	(21)
5052-H32	722 (2370 ft.)	.5	0.002	0.09	0.66	26	----	----	----	----		
5052-0	722 (2370 ft.)	1	0.010	0.4	0.00	0	----	----	0.51	20	Port Hueneme, Calif.	(15)
5052-H32	722 (2370 ft.)	1	----	----	Few	Few	----	----	0.00	0		
5052-H34	722 (2370 ft.)	1	0.005	0.2	I (1)	I	----	----	0.86	34	Port Hueneme, Calif.	(7)
5052	722 (2370 ft.)	1	0.005	0.2	0.31	12	0.20	8	----	----		
5052-H32	1280 (4200 ft.)	1	<0.254	<10	<0.25	<10	----	----	----	----	Tongue-of-the- Ocean, Bahamas	(7)
5052-H32	1280 (4200 ft.)	1	<0.254	<10	<0.25	<10	----	----	----	----		
5052-H32	1280 (4200 ft.)	1	<0.254	<10	<0.25	<10	----	----	----	----		
5052-H32	1280 (4200 ft.)	1	<0.254	<10	<0.25	<10	----	----	----	----		
5052-0	1615 (5300 ft.)	3	0.079	3.1	0.00	0	----	----	1.65	65 (PR)	Port Hueneme, Calif.	(12-14)
5052-0	1719 (5640 ft.)	.3	0.094	3.7	0.00	0	----	----	1.65	65 (PR)		
5052-0	1719 (5640 ft.)	.3	<0.003	<0.1	Severe	Severe	----	----	0.00	0	Port Hueneme, Calif.	(12-14)
5052-H34	1719 (5640 ft.)	2	0.056	2.2	1.65	65 (PR)	----	----	1.65	65 (PR)		
5052-H34	1719 (5640 ft.)	2	----	----	----	----	----	----	0.00	0	Port Hueneme, Calif.	(12-14)
5052-0	2067 (6780 ft.)	1	0.114	4.5	0.00	0	----	----	1.58	62 (PR)		
5052-H32	2067 (6780 ft.)	1	----	----	0.99	39	----	----	0.00	0		

(1) Incipient

TABLE XI

PERFORMANCE OF ALCLAD ALLOYS IN DEEP SEA WATER (1)

Alloy	Depth (m)		Time (Yrs.)	Rate		Max. Pit Depth		Avg. Pit Depth		Freq. (Pits/ cm ²)	Crevice Depth		% Clad Consumed
				(mm/yr)	(mpy)	(mm)	(mils)	(mm)	(mils)		(mm)	(mils)	
Alc. 3003-H12	713	(2340 ft.)	0.5	0.056	2.2	0.38	15	0.33	13.1	0.43	0.33	13	Large area
Alc. 3003	713	(2340 ft.)	0.5	0.058	2.3	0.00	0	----	----	----	0.00	0	General
Alc. 3003-H12	722	(2370 ft.)	1	0.056	2.2	0.36	14	0.33	12.9	0.33	0.38	15	20%
Alc. 3003	722	(2370 ft.)	1	0.041	1.6	0.00	0	----	----	----	0.00	0	60%
Alc. 3003-H12	1615	(5300 ft.)	3	0.018	0.7	0.51	20	0.42	16.5	0.06	0.33	13	18%
Alc. 3003-H12	1615	(5300 ft.)	3	0.008	0.3	0.38	15	0.38	14.8	0.03	----	----	Large area
Alc. 3003	1615	(5300 ft.)	3	0.038	1.5	0.00	0	----	----	----	0.00	0	General
Alc. 3003-H12	1719	(5640 ft.)	0.3	0.005	0.2	0.46	18	0.37	14.6	0.02	0.38	15	Large area
Alc. 3003-H14	1719	(5640 ft.)	0.3	----	----	I	I(2)	----	----	----	0.00	0	----
Alc. 3003	1719	(5640 ft.)	0.3	0.069	2.7	0.0	0	----	----	----	0.00	0	General
Alc. 3003-H12	1719	(5640 ft.)	2	0.008	0.3	0.33	13	0.33	12.8	< 0.02	0.33	13	18%
Alc. 3003-H14	1719	(5640 ft.)	2	----	----	0.00	0	----	----	----	0.00	0	General
Alc. 3003	1719	(5640 ft.)	2	0.036	1.4	0.00	0	----	----	----	0.00	0	General
Alc. 3003-H12	2067	(6780 ft.)	1	0.010	0.4	0.33	13	0.33	13	0.03	0.35	14	----
Alc. 3003	2067	(6780 ft.)	1	0.064	2.5	0.00	0	----	----	----	0.00	0	General

(1)

LocationReference

Port Hueneme, Calif.

(12-14)

(2)

Incipient

TABLE XII

COMPOSITION OF SYNTHETIC SEA SALT (LAKE PRODUCTS)

<u>Compound</u>	<u>% By Weight *</u>
NaCl	58.49
Mg ₂ Cl ₂ ·6 H ₂ O	26.46
Na ₂ SO ₄	9.750
CaCl ₂	2.765
KCl	1.645
NaHCO ₃	0.477
KBr	0.238
H ₃ BO ₃	0.071
SrCl ₂ ·6H ₂ O	0.095
NaF	0.007

* 41.953 grams to make 1 liter of synthetic sea water

TABLE XIII

NOMINAL COMPOSITION OF ALUMINUM ALLOYS

	<u>Si</u>	<u>Mn</u>	<u>Mg</u>	<u>Cr</u>
1100	----	----	----	----
3003	----	1.2	----	----
5052	----	----	2.5	0.25
6063	0.4	----	0.7	----

TABLE XIV

SPECIMEN SIZES FOR AMMONIA CORROSION TESTS

Specimen Size		Area		A/V (cm ⁻¹)
(cm)	(in.)	(cm ²)	(in. ²)	
1.3 x 0.64 x 0.163	0.5 x 0.25 x 0.064 *	2.2	0.34	0.0028
10.1 x 1.3 x 0.163	4 x 0.5 x 0.064	29.5	4.57	0.037
12.1 x 4.1 x 0.163	4.75 x 1.5 x 0.064	103	16.0	0.131
11.4 x 6.4 x 0.163	4.5 x 2.5 x 0.064	151	23.4	0.189
12.1 x 8.3 x 0.163	4.75 x 3.25 x 0.064	206	31.9	0.258

* Thickness of 6063 alloy specimens 0.241 cm (0.095 in.)

TABLE XV

RATES AND TYPE OF ATTACK OF ALLOYS EXPOSED TO AMMONIA-SEA WATER
SOLUTIONS

Ammonia Concentration, %	Initial Corrosion Rate		Final Corrosion Rate			Type of Attack
	(mmpy)	(mpy)	(mmpy)	(mpy)		
5	0.533	21	0.000	0.0	*	General
10	0.305	12	0.066	2.6	*	General
30	-----	--	0.013	0.53	*	Superficial Etching
50	-----	--	0.006	0.23		Superficial Etching
70	-----	--	0.002	0.08		Superficial Etching
90	-----	--	0.022	0.85		Pitting
95	-----	--	0.036	1.4		Pitting
100	0.048	1.9	0.000	0.0		Pitting

* Specimens exposed separately.

TABLE XVI

DEPTH OF PITTING ATTACK OF ALLOYS EXPOSED IN 90% TO 100%
AMMONIA-SEA WATER SOLUTIONS

Alloy	% NH ₃	Time (Wks.)	Max. Pit Depth		Avg. Pit Depth	
			(mm)	(mils)	(mm)	(mils)
1100	100	1	0.04	1.5	0.02	0.9
		2	0.03	1.2	0.02	0.76
		4	0.04	1.6	0.02	0.95
1100	95	1	0.01	0.35	0.01	0.22
		2	0.01	0.57	0.01	0.37
		4	0.01	0.47	0.01	0.36
1100	90	1	0.01	0.35	0.01	0.29
		2	0.01	0.43	0.01	0.28
		4	0.01	0.38	0.01	0.26
3003	100	4	0.12	4.7	0.03	1.2
5052	100	4	0.06	2.3	0.03	1.3
6063	100	4	0.02	0.6	0.01	0.3

Figure 1. Weight loss required for passivation (■) and initial rates of attack (○) of 1100 alloy in ammonia-water solutions.

Figure 2. Performance of 1100 Alloy in Surface Sea Water

Figure 3. Performance of 3003 Alloy in Surface Sea Water

Figure 4. Performance of 5052 Alloy in Surface Sea Water

Figure 5. Performance of 6063 alloy in surface sea water.

20X

Figure 6. Cross sectional view of Alclad 3003 heat exchanger tube wall showing maximum cladding penetration after 10 years service in lube oil system aboard the S. S. Alcoa Clipper.

Figure 7. Performance of 1100 Alloy in Deep Sea Water

Figure 8. Performance of 3003 Alloy in Deep Sea Water

Figure 9. Performance of 5052 Alloy in Deep Sea Water

Figure 10. Schematic of Ammonia Distillation Apparatus

Figure 11. Schematic illustrating method of ammonia transfer to pressure vessel.

Figure 12. Schematic of flow test apparatus

Figure 13. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 (Δ) and 6063 ($\circ$) alloys exposed individually (closed) and together (open) in 5% ammonia-95% sea water solution.

Figure 14. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 (Δ) and 6063 ($\circ$) alloys exposed individually (closed) and together (open) in 10% ammonia - 90% sea water solution.

Figure 15. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 (Δ) and 6063 ($\circ$) alloys exposed individually (closed) and together (open) in 30% ammonia - 70% sea water solution.

Figure 16. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 (Δ) and 6063 ($\circ$) alloys exposed together in 50% ammonia - 50% sea water solution.

Figure 17. Weight loss versus time for 1100 (□), 3003 (▽), 5052 (△) and 6063 (○) alloys exposed together in 70% ammonia - 30% sea water solution.

Figure 18. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 ($\triangle$) and 6063 ($\circ$) alloys exposed together in 90% ammonia-10% sea water solution.

Figure 19. Weight loss versus time for 1100 (□), 3003 (▽), 5052 (△) and 6063 (○) alloys exposed together in 95% ammonia-5% sea water solution.

Figure 20. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 (Δ) and 6063 ($\circ$) alloys exposed together in 100% liquid ammonia containing 1X sea salt.

A. 1100

7 Days

14 Days

30 Days

B. 6063

7 Days

14 Days

30 Days

C.

30 Days

1100

3003

5052

6063

Figure 21. Surface photographs (1X) of the alloys exposed in 100% ammonia containing sea salt.

Figure 22. Weight losses for 1100 (□), 3003 (▽), 5052 (Δ) and 6063 (○) alloys exposed together for one month in 0 to 100% ammonia-sea water solutions.

Figure 23. Total weight loss for various area 1100 alloy specimens exposed one month in 0 to 30% ammonia - deionized water solutions.

Figure 24. Total weight loss for various area 1100 alloy specimens exposed one month in 0 to 30% ammonia-sea water solutions.

Figure 25. Total weight loss (mg/cm^2) as a function of specimen area for 1100 alloy exposed in 5% (O), 10% (Δ) and 30% ($\square$) ammonia-sea water solutions.

Figure 26. Surface photograph (1X) of 3003 alloy tubing exposed in 5% ammonia - 95% sea water flowing at (A) 1.2 m/sec (4 ft./sec.) and (B) 2.4 m/sec. (8 ft./sec.).

Figure 27. Galvanic currents for 1100 alloy coupled to T-1, 316 stainless and mild steels and 3003 alloy coupled to mild steel (24) in air contaminated liquid ammonia (currents with respect to the aluminum).

SEM

20X

Figure 28. Surface view showing round bottom type pitting of 1100 alloy which was galvanically coupled to 316 stainless steel in air contaminated liquid ammonia.

Figure 29. Galvanic currents (O) and potential differences (Δ) for 3003 alloy coupled to mild steel in air contaminated liquid ammonia containing 0 to 10% H_2O . (Current with respect to the aluminum.) (24)

Figure 30. Galvanic currents for 1100 alloy coupled to mild and 316 stainless steels in deaerated liquid ammonia. (Currents with respect to the aluminum).

Figure 31. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 (Δ) and 6063 ($\circ$) alloys exposed together in 1X sea water under 7.6×10^5 Pa (110 psig) Freon 22.

Figure 32. Weight loss versus time for 1100 ($\square$), 3003 (∇), 5052 (Δ) and 6063 ($\circ$) alloys exposed together in 1X sea water under 7.6×10^5 Pa (110 psig) propane.