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REVERSING SENSITIZATION OF NATURALLY EXFOLIATED 5456-H116 ALUMINUM ALLOYS

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Key words: sensitization, β phase, corrosion, Al_3Mg_2, 5456-H116.

ABSTRACT

5456-H116 Al-Mg alloy has been broadly used in the U.S. Navy in order to meet the demand of reducing ship hull weight while considering high specific strength, corrosion resistance, and weldability. A particular concern of these alloy is sensitization, which causes it to be sensitized when highly anodic β phase (Al_3Mg_2) is precipitated at grain boundaries especially in service exceeding 65~200°C, leading to intergranular corrosion (IGC), exfoliation and stress corrosion cracking (SCC). This study investigated the reversal of sensitization of a naturally exfoliated 5456-H116 alloy plate by planned heating treatment with a short exposure to 250°C. The properties of sensitized specimens of 5456-H116 were investigated using microhardness testing, electrochemical measurements, Nitric Acid Mass Loss Testing (NAMLT), optical microscopy, and Scanning Electron Microscopy (SEM). The results reveal that the corrosion resistance of the stabilized specimens approached those of the unsensitized plates, and their mechanical strength was not adversely affected during the recovery process. Therefore, in-service plates can be refurbished by stabilizing heat treatment rather than replacement, potentially reducing maintenance costs.

I. INTRODUCTION

5xxx Al-Mg alloys are medium-strength, non-heat-treatable wrought aluminum alloys that have been extensively used in marine structures owing to their lightweight, weldability and favorable corrosion resistance. The U.S. Navy has preferred using magnesium-strengthened 5xxx series (including 5083, 5086 and 5456) since the 1950s [16, 17]. However, 5xxx Al-Mg alloys that contain more than 3wt.% Mg can be sensitized, becoming susceptible to intergranular corrosion (IGC), when exposed to elevated temperatures and are not regarded as suitable for service above 65°C [5-10, 13-15]. Since the β phase is electrochemically more active than the alloy matrix, plates with a sensitized microstructure are susceptible to intergranular corrosion, exfoliation, and stress corrosion cracking (SCC) when exposed to a stressful and corrosive environment. The U.S. Navy has observed IGC and SCC in the 5456-H116 aluminum superstructures of the Perry class frigate (FFG-7) and the Ticonderoga class cruiser (CG-47) where cracks extending several feet long have been reported [16]. During 2001 and 2002, over 200 commercial vessels that were constructed of aluminum alloy 5083-H321 experienced severe pitting and extensive SCC, which caused these vessels to be unfit for traveling at sea [3]. To solve the problem of IGC, the American Society of Testing and Materials (ASTM) developed a new specification for marine-grade aluminum alloys – ASTM B928 [1]. This specification superseded ASTM B 209 for all high magnesium (≥ 3wt.%) alloys and tempers that are intended specifically for marine applications. ASTM B928 requires certification of aluminum alloys for marine use beyond ASTM G67 nitric acid mass loss testing (NAMLT) [2], to evaluate clearly its susceptibility to IGC. In the tests that are demanded by the specifications, nitric acid dissolves the β phase, eventually causing the grains that are surrounded by a relatively continuous network of β phase to fall out, resulting in significant mass loss from the test sample. At temperatures within the effective service envelope for these alloys (e.g., below 50°C), the remaining β phase precipitates on the grain boundaries over long periods [14]. Accordingly, in service, the 5xxx Al-Mg alloys that meet the B928 requirements still develop a sensitized microstructure, especially in the heat-affected zone (HAZ) of welds [18], or in deck and superstructure applications when exposed to solar radiation [4]. Several of these corroded vessels currently require new hulls and superstructures and are now facing significant maintenance costs.

To solve these problems of the sensitization of marine-grade aluminum plates, stabilization heat treatment has been used to restore the corrosion resistance of some naturally exfoliated marine-grade alloy specimens by reducing their sensitization, thereby extending their service lives [11]. As illustrated in the phase diagram shown in Fig. 1 [12], marine-grade alloys such as 5086 (3.5~4.5 Mg), 5083 (4.0~4.9 Mg)

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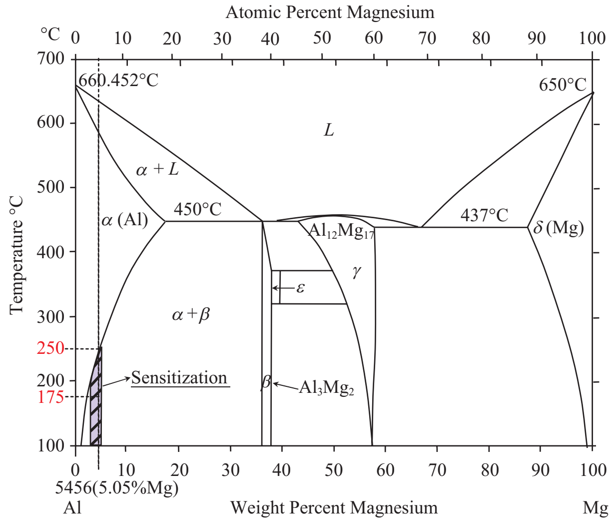

Fig. 1. Phase diagram of the Al-Mg binary system with the composition of marine-grade alloys sensitization region indicated [12].

and 5456 (4.7~5.5 Mg) become sensitized and therefore susceptible to corrosion upon exposure to a temperature in the range that is indicated by the hashed area ($\alpha + \beta$ phase). Fig. 1 also reveals that these alloys can be annealed at temperatures above the β phase solid solubility limit, such that the β phase can be re-dissolved in the α matrix and not form a continuous network along the grain boundaries. However, the annealing temperature and time must be maintained in the recovery stage to prevent softening of the plate. In effect, a sensitization reversing treatment can be used as a basis for developing a remedial process – an on-site heat treatment that is applied to ships' superstructures as an alternative to the costly method of repair by replacing sensitized plates or entire structures.

II. EXPERIMENT

1. Material

The material that was used in this study was a naturally exfoliated 5456-H116 plate (6 mm thick) that was sampled from the superstructure of a PFG2 class frigate (Perry class ship in Taiwan's Navy), which had been in service for around 20 years and experienced various degrees of exfoliation, ranging from barely visible to extensive. The chemical composition of the plate was measured by glow discharge spectrometer (GDS) and the weight percentages are given in Table 1.

2. Heat Treatment

To investigate the effects of annealing temperature, the as-received specimens were annealed in the temperature range of 25~450°C for 10, 30, 60 and 180 minutes. According to Fig. 1 and Oguocha *et al.* [13], the limiting temperatures for stabilization and critical sensitizing of the specimens were about 250°C and 175°C, respectively. Holding the specimens at 250°C for 10, 30, 60 and 180 minutes was found to effectively

Table 1. Chemical composition of the naturally exfoliated 5456-H116 plate used in this study (in wt.%).

Mg	5.05
Mn	0.60
Cr	0.08
Fe	0.23
Si	0.08
Cu	0.03
Ti	0.01
Zn	0.05
Zr	0.07
Al	Rest

restore their corrosion resistance as indicated by their meeting the NAMLT requirements: ASTM B928 (<15 mg/cm^2). Specimens that were heated at 175°C remained sensitized for 10, 30, 60 and 180 minutes.

3. Microhardness Testing

Microhardness testing was conducted to quantify strength, determine the extent of softening caused by annealing and to determine whether an excessive treatment temperature had been used. An HVS-1000 Vickers microhardness tester was employed with a load of 150 g applied for 15 seconds. Ten microhardness readings were taken from each sample to ensure representative results.

4. NAMLT Testing

Nitric acid mass loss testing (NAMLT) was employed to examine the IGC susceptibility of the annealed specimens. The specimens were cut into 50 mm × 50 mm × 6mm (L × T × S) and prepared in accordance with ASTM G67 [2], which consisted of immersing test specimens in concentrated (70%) nitric acid at 30°C for 24 hours and determining the mass loss per unit area as a measure of susceptibility to intergranular corrosion. The mass loss per unit area reported in this study was the average of three tests for each annealing condition.

5. Electrochemical Measurement

An electrochemical approach (Linear Polarization Resistance-LPR) was utilized to determine the corrosion resistance following stabilization treatment and verify the absence or presence of a sensitized microstructure. Electrochemical measurements were carried out in a three-electrode system. The experimental set-up was comprised of a platinum counter electrode, 1 cm^2 of the specimen as working electrode, and a saturated calomel reference electrode (SCE). The electrolytes were 3.5 wt.% sodium chloride (NaCl) solution at pH 7 for the open circuit potential (OCP) measurement, which was carried out to record the mixing potential versus reaction time (E_{ocp} *vs*. time). All the specimens were immersed in 3.5 wt% NaCl solution for 30 minutes to ensure stability of OCP. The measurements were performed using an Autolab PGSTAT30 in the range of −1.0 to +0.2 V *vs*. OCP at a scan rate 5 mV/s.

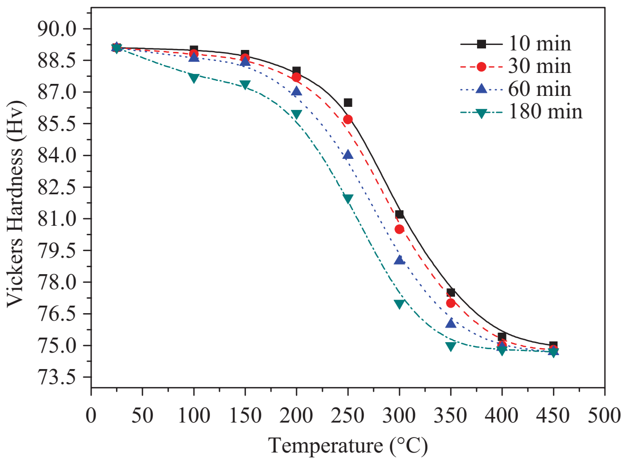

Fig. 2. Variation of hardness with heat treatment conditions for the naturally exfoliated 5456-H116 plate.

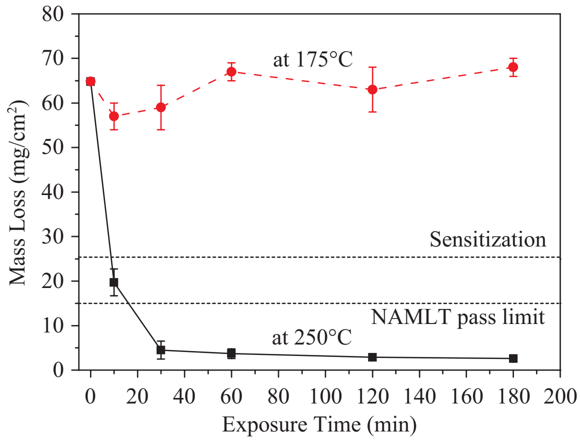

Fig. 3. NAMLT test (immersion into HNO_3 for 24 h) results of the 5456-H116 samples after being treated in the stabilization and sensitizing temperature for 10, 30, 60, 120, and 180 minutes.

6. Microstructure Observations

The microstructural features of the specimens were studied using a Topcon ABT-60 scanning electron microscope (SEM) and an optical microscope (OM). The presented photographs display the longitudinal-short transverse (L-ST) orientation at the mid-thickness (t/2) location of the specimen. Metallographic specimens were etched using a 5% hydrofluoric acid solution. We consider a sensitized microstructure as one with a semi-continuous or continuous network of precipitates at grain boundaries.

III. RESULTS AND DISCUSSION

Fig. 2 presents the results of the hardness tests of samples that were heat-treated at 25~450°C. The hardness value in each annealing condition was the average of ten tests. The hardness decreased as the temperature or duration of heat treatment increased. These curves revealed that annealing at 25~250°C slightly reduced hardness throughout the recovery process. Significant changes in hardness occurred upon treatment between 250°C and 350°C, and were caused by recrystallization, which was affected by the annealing temperature and time. Hence, the basic softening process occurred at temperatures in the range of 250~400°C. The steady hardness values upon annealing at temperatures between 400 and 450°C indicated that the coarsening of recrystallized grains had little impact on hardness. Therefore, the hardness of the annealed samples was clearly dominated by the fraction of the recrystallized grains rather than the rate of coarsening of the recrystallized grains. As a result, the effective range of temperatures for stabilization treatment is approximately 240~250°C.

Fig. 3 presents the NAMLT test results. Following treatment at 250°C for over 30 minutes, the naturally exfoliated and sensitized specimens reverted to having low NAMLT test values that approached those of unsensitized plates. However, the specimens that were treated at 175°C retained high

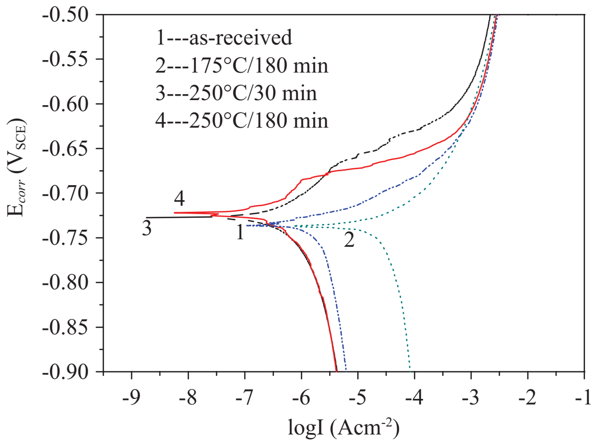

Fig. 4. Potentiodynamic polarization curves for the naturally exfoliated 5456-H116 alloy annealed at 175°C for 180 minutes and at 250°C for two time periods: 30 and 180 minutes (measured in 3.5% NaCl solution, scanning rate is 5 mV/s).

NAMLT test values. The failed samples with NAMLT results above 25 mg/cm^2 required an exposure time of 10~30 minutes at 250°C for the stabilization treatments to reduce these results to below 15 mg/cm^2.

Fig. 4 plots the potentiodynamic polarization curves of the tested specimens. They show that their corrosion resistance was improved by treatment at 250°C for 30 and 180 minutes, but were steadily worsened upon treatment at 175°C for 180 minutes. Evidently the corrosion current densities of the specimens that were treated at 250°C for 30 and 180 minutes were almost the same and lower than that of the as-received specimen. The values for the corrosion potential (E_{corr}) was estimated from the intersection of the anodic Tafel lines (Table 2). It can be seen that the corrosion potential values annealing at 250°C for 30 minutes shifted to the positive direction as compared to that of annealing at 175°C for 180 minutes. These are the typical features of better corrosion resistance,

Table 2. Corrosion potentials obtained from polarization curves of the naturally exfoliated 5456-H116 plate.

Exposure condition	$E_{corr}(V_{SCE})$
1. as-receive	-0.7362
2. 175°C/180 minutes	-0.7370
3. 250°C/30 minutes	-0.7275
4. 250°C/180 minutes	-0.7225

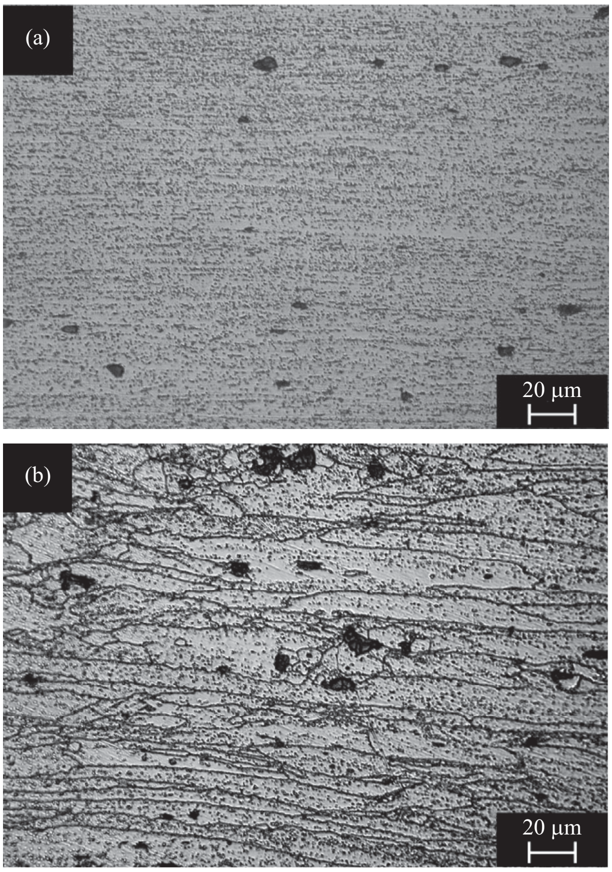

Fig. 5. Microstructures with variations in continuity of matrix grain boundary and β precipitation: (a) unsensitized 5456-H116, showing undetectable grain boundary, (b) naturally exfoliated 5456-H116, showing continuous network of grain boundary.

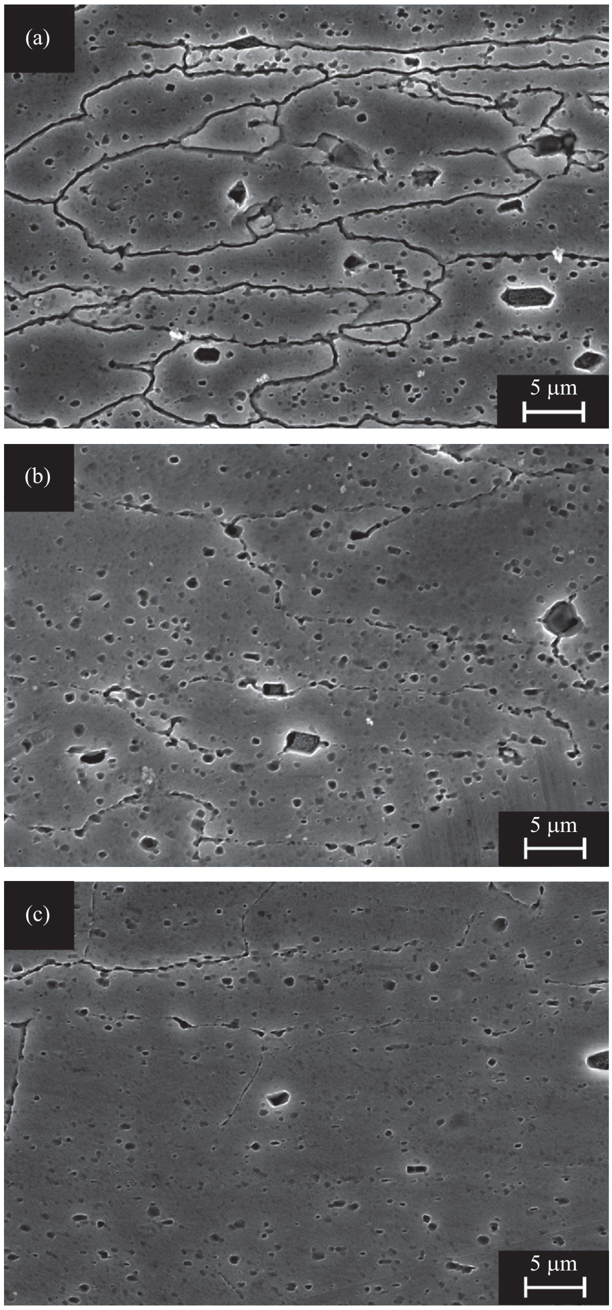

Fig. 6. SEM micrograph showing the effect of stabilization heat treatment on the microstructure of the as-received specimen and specimens annealed at 250°C for different lengths of time: (a) as-received, (b) 10 minutes, (c) 30 minutes.

and this result shows good corrosion resistance properties after 250°C annealing treatment. The above results indicate that the effective stabilization temperature may drop slightly as the exposure duration is increased. The specimens remain sensitized below this range whereas hardness and strength are significantly reduced above this range.

As shown in Fig. 5 and Fig. 6, optical and SEM micrographs confirm that the stabilization treatment results in the formation of a discontinuous or semi-continuous network of grain boundary precipitation, as expected from the NAMLT results. Fig. 5(a) presents the typical microstructure of 5456 alloy in the rolling direction. The microstructure is characterized by irregularly shaped intermetallic particles and their heterogeneous distribution on the surface. Fig. 5(b) shows the evidently continuous networks of β phase precipitates along the grain boundaries in the naturally exfoliated samples with a unrecrystallized structure. After short exposure (10~30 minutes) at 250°C, the β precipitation on the grain boundaries merge back into solution (Figs. 6(a)~6(c)), and the sensitized naturally exfoliated specimens revert to having low NAMLT test values, which approach those of unsensitized plates, if the exposure time exceeds 30 minutes. However, in the alloys

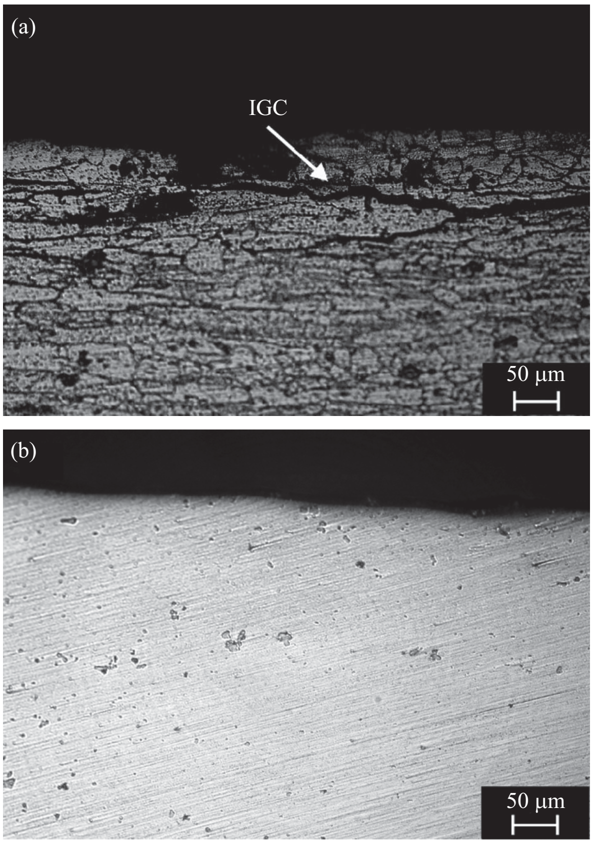

Fig. 7. Optical micrographs of the naturally exfoliated 5456-H116 specimens: (a) as-received, and (b) heat-treated at 250°C for 30 minutes, and then immersed in 70% HNO_3 for 24 h.

treated at 175°C, whether for 10 minutes or 3 hours, the β phase is still precipitated as a continuous network along the boundaries and the sensitized specimens retain a high NAMLT test value.

Fig. 7 presents the microstructures of two specimens that were naturally exfoliated upon immersion in concentrated (70%) HNO_3 at 30°C for 24 hours. The acidic corrosive environment resulted in intensive intergranular attack (Fig. 7(a)) along the edge of the as-received specimen. However, brief heat-treatment at 250°C for 30 minutes (Fig. 7(b)) resulted in smoothing of the edge without any evidence of intergranular corrosion.

IV. CONCLUSIONS

The corrosion resistance of 5xxx marine-grade alloy is excellent, as this alloy eventually becomes sensitized and susceptible to IGC and SCC under long-term service at high temperatures above 65°C. However, a new thermal process was herein developed to reverse the sensitization of naturally exfoliated 5456-H116 aluminum alloys and effectively stabilize them in a non-sensitized state. This process consisted of exposing the sensitized plate at 250°C for periods as short as 10~30 minutes; a heating process which does not adversely affect their hardness. This improved method, achieved by a simple thermal process, will enable the service life of ships to be extended while reducing maintenance costs and preventing SCC that would otherwise be caused by sensitization.

REFERENCES

1. ASTM B928, *Standard Specification for High Magnesium Aluminum-Alloy Sheet and Plate for Marine Service and Similar Environments*, ASTM International, West Conshohocken, PA (2009).
2. ASTM G67, *Standard Test Method for Determining the Susceptibility to Intergranular Corrosion of 5XXX Series Aluminum Alloys by Mass Loss After Exposure to Nitric Acid (NAMLT Test)*, ASTM International, West Conshohocken, PA (2004).
3. Bushfield, H., Cruder, M., Farley, R., and Towers, J., "Marine aluminum Plate - ASTM standard specification B928 and the events leading to its adoption," World Maritime Technology Conference, San Francisco, CA (2003).
4. Czyryca, E. J. and Hack, H. P., *Corrosion of Aluminum Alloys in Exfoliation-Resistant Tempers Exposed to Marine Environments for 2 Years*, Report No. 4432, Naval Ship Research and Development Center, Annapolis, MD, U.S.A. (1974).
5. Goswami, R. and Holtz, R. L., "Transmission electron microscopic investigations of grain boundary beta phase precipitation in Al 5083 aged at 373°K (100°C)," *Metallurgical and Materials Transactions A*, Vol. 44, No. 3, pp. 1279-1289 (2013).
6. Goswami, R., Spanos, G., Pao, P. S., and Holtz, R. L., "Precipitation behavior of the β phase in Al-5083," *Materials Science and Engineering A*, Vol. 527, Nos. 4-5, pp. 1089-1095 (2010).
7. Goswami, R., Spanos, G., Pao, P. S., and Holtz, R. L., "Microstructural evolution and stress corrosion cracking behavior of Al-5083," *Metallurgical and Materials Transactions A*, Vol. 42, No. 2, pp. 348-355 (2011).
8. Holtz, R. L., Pao, P. S., Bayles, R. A., Longazel, T. M., and Goswami, R., "Corrosion-fatigue behavior of aluminum alloy 5083-H131 sensitized at 448°K (175°C)," *Metallurgical and Materials Transactions A*, Vol. 43, No. 8, pp. 2839-2849 (2012).
9. Jain, S., Lim, M. L. C., Hudson, J. L., and Scully, J. R., "Spreading of intergranular corrosion on the surface of sensitized Al-4.4Mg alloys: A general finding," *Corrosion Science*, Vol. 59, pp. 136-147 (2012).
10. Jones, R., Baer, D., Danielson, M., and Vetrano, J., "Role of Mg in the stress corrosion cracking of an Al-Mg alloy", *Metallurgical and Materials Transactions A*, Vol. 32, No. 7, pp. 1699-1711 (2001).
11. Kramer, L., Phillippi, M., Tack, W. T., and Wong, C., "Locally reversing sensitization in 5xxx aluminum plate," *Journal of Materials Engineering and Performance*, Vol. 21, No. 6, pp. 1025-1029 (2012).
12. Massalski, T. B., Murray, J. L., Bennett, L. H., and Baker, H., *Binary Alloy Phase Diagrams*, ASM International, Metals Park, OH, pp. 129-131 (1984).
13. Oguocha, I. N. A., Adigun, O., and Yannacopoulos, S., "Effect of sensitization heat treatment on properties of Al-Mg alloy AA5083-H116," *Journal of Materials Science*, Vol. 43, No. 12, pp. 4208-4214 (2008).
14. Reboul, M. and Baroux, B., "Metallurgical aspects of corrosion resistance of aluminum alloys," *Materials and Corrosion*, Vol. 62, No. 3, pp. 215-233 (2011).
15. Scamans, G., Holroyd, N., and Tuck, C., "The role of magnesium segregation in the intergranular stress corrosion cracking of aluminum alloys," *Corrosion Science*, Vol. 27, No. 4, pp. 329-347 (1987).
16. Schwarting, R., Ebel, G., and Dorsch, T. J., "Manufacturing techniques and process challenges with CG47 class ship aluminum superstructures modernization and repairs," Fleet Maintenance and Modernization Symposium 2011, San Diego, CA (2011).
17. Sielski, R. A., "The history of aluminum as a deckhouse material," *Naval Engineers Journal*, Vol. 99, No. 3, pp. 165-172 (1987).
18. Sielski, R. A., "Research needs in aluminum structure," *Ships and Offshore Structures*, Vol. 3, No. 1, pp. 57-65 (2008).