

PROBLEMS AND PROSPECT OF Al-Mg ALLOYS APPLICATION IN MARINE CONSTRUCTIONS

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ABSTRACT

The position of steel as the most widely used material in the shipbuilding industry originates from the superior mechanical properties and low manufacturing costs. The increasing demands for lowering the weight of different ships due to the increase of their sizes or generally increasing the payload, the application of Al – alloys offered the potential to lower the weight of structures by over 50% in comparison with those made of low-carbon steel. The roughly five times higher costs of Al – alloys production in respect to the costs of low-carbon steel become acceptable in a certain relations between the total cost increase on one hand, and payload increase as well as the excellent corrosion resistance, on the other hand. The evolution of ship performances promoted the need for the development of new Al – alloys with improved mechanical properties, corrosion resistance, weldability, etc. In this paper the current efforts in alloys modifications for improving their marine service ability were considered, and assessment was made on the potential of the different aluminum alloy types for marine applications. The non-heat-treatable Al-Mg alloys were appointed as favorable ones in respect to the costs and all the required properties for successful vessel service. The paper deals with the current problems appeared in the aluminum marine service and with the metallurgical aspects of structure and property control which is necessary to ensure the successful applications.

Keywords: Al-alloys, microstructure, corrosion, marine application

Historical notes

Structural steel is a traditional material used over 150 years in the shipbuilding industry because of excellent mechanical properties and low manufacturing costs. Due to the increasing demand for building the larger ships, designers had to search for alternative materials in order to reduce the weight of ships. Aluminum and its alloys were assessed as a possible replacement for steel, due to a high corrosion resistance and a potential of considerable weight saving, as its density is almost three times lower than the density of steel (2.73 g/cm³ for aluminum vs. 7.85 g/cm³ for steel). Finally, the technological progress allowed aluminum alloys to approach the minimum of required mechanical properties in shipbuilding provided by low carbon steel. Those points had a decisive role in considering aluminum alloys as a promising material for marine applications.

The appearance of aluminum alloys as an alternative material in boat and ship constructions is related to the 1960's [1]. Smaller boats as police or patrol boats, fishing vessels, fire boats or fast passenger vessels as catamarans (up to 400 passengers) were typical in Europe, North America and especially in Asia [2]. The development of larger vessels based on aluminum alloys is related to the appearance of first 68 m long all aluminum ship ("Aluminia") in Germany [1], with a cargo capacity of 1000 tonnes. Later, in 1967, a 69 m long trailer ship was constructed in USA [3], etc.

Steel replacement with aluminum alloys

Weight reduction.

The major drawback of using steel in ship constructions is the weight. After proper design of smaller structures made of low-carbon steel, the weight reduction of about 50% can be achieved by introducing of aluminum [4]. In case of superstructures or even hulls of ships it can be over 60% [5]. Accordingly it directly reduces the loss of cargo dead weight due to the structure. The weight saving improves the ship stability – allowing design of narrower ships [6], as well as the fuel efficiency becomes an important goal, especially in larger ships.

Mechanical properties.

The structural steels used in shipbuilding are generally represented by the group of normal strength carbon steels and by the high strength HSLA steels. The minimum of required mechanical properties, defined by "Unified Rules" from 1980 [7], are shown in Table 1. Besides those levels of properties, a family of HSLA type steels HY-80, HY-100 or HY-130 with yield strengths of 550 MPa, 690 MPa and 900 MPa, respectively, is the only choice for marine application where the strength level is critical as the hulls and superstructures of battleships, aircraft carriers, submarines etc. The most popular and most widely used structural steel in shipbuilding is the A36 type (according to ASTM designation) with a typical yield stress of 250 MPa.

Table 1. Mechanical properties of steels for marine applications [7]

Steel	YS (min.)	UTS (min.)	Elongation A ₅ (min.)	Toughness* (min.) KCV, Jcm ²		
	MPa	MPa	(%)	L	T	°C
Normal strength carbon steel	235	400-490	22	27	20	0
						- 10
						- 40
High strength HSLA steels	315	470-590	22	31	22	0
						- 20
						- 40
	355	490-620	21	34	24	0
						- 20
						- 40

*ISO V notch samples

The mechanical properties or even corrosion resistance of this type of carbon steel were improved by adding a small amount of alloying elements as manganese, vanadium or chromium.

The properties of typical aluminum alloys for marine applications are shown in Table 2. It is clear that the carbon steels from the group of normal strength and the aluminum alloys in conditions for marine application have strength parameters of same order, while those of HSLA steels are several times higher. So, it seems that the carbon steels of normal strength can be replaced by aluminum alloys in the range limited by their application, while in case of the use of high strength HSLA steels it is not possible.

Table 2. Typical mechanical properties of aluminum alloys for marine applications

Al-alloys		YS	YS/UTS after welding	UTS	Elongation	Fracture Toughness
Type AA	Temper	(MPa)	(MPa)	(MPa)	(%)	(MPa√m)
5083	H116/H321	215	125/275	305	10	43
5383	H116/H321	220	145/290	305	10	
5383NG	H116/H321	220	160/290	305	12	
5456	H116/H321	255		350		
5059 "Alustar"	H116/H321	270	160/330	370	10	
5086	H116	207		290	12	49
6082	T6	260	115/205	310	8-10	
6005A	T6	225		270	8	

Corrosion resistance

Carbon and low-alloy steels are not resistant to corrosion attack in aggressive environments such as seawater. They need a proper surface protection as painting or other type of coatings which should be regularly repeated. On the other hand, aluminum corrodes over 100 times slower than the carbon steels. The excellent corrosion resistance of aluminum originates from the tightly bonded oxide film formed on the surface when it is exposed to air or water. Even such a very well adhering oxide film can fail in salt water, allowing a certain degree of corrosion. The most popular aluminum alloys for use in corrosive environments are non-heat treatable 5000, and heat-treatable 6000 type alloys, because of well balanced strength parameters, weldability and formability. The

6000 alloys are stronger but two-three times less corrosion resistant than the 5000. The little or no need for maintenance of marine structure surfaces (less frequent painting or other coating refreshments) make an important cost saving during the service – life of any aluminum component [9].

Cost analysis.

Besides the strength constraint in cases of highly stressed constructions, where high strength steels are unavoidable, the second disadvantage is related to the fact that the aluminum cost is roughly five times higher than the steel's. So, because of high cost, it seems that aluminum is not always economical. However, it was assessed that taking into account the weight reduction, high corrosion resistance and satisfying strength level, the replacement of conventional – normal strength structural steels with aluminum alloys is feasible in the shipbuilding industries [2, 6]. This replacement is economical if all the aluminum advantages are carefully integrated in new design approach for every type of boat or ship. It is worth of note that in an overall cost analysis of steel replacement in the car industry [8], it was estimated that there is a potential for at least 10% lower costs for the non-heat-treatable alloys due to less expensive production compared to the heat-treatable types. That point can give an important advantage for to the development of 5000 type alloys for shipbuilding applications.

The basic approach concerning the steel replacement was summarized earlier, understanding all the benefits and limitations as follows [6]:

"It cannot be emphasized too strongly that aluminum as a new shipbuilding material needs treating as such. It has its own design problems, its own maintenance problems, and its own repair problems. It cannot be used everywhere as a substitute for steel or other alloy, but if the contractors, naval architects, shipwrights, and shipbuilders, and of course suppliers will treat it as something that requires a new approach they will find they have a very fine metal for use in seawater and marine atmospheres".

Selection of aluminum alloys

The traditional and the most often used Al-alloys in shipbuilding are 5083 type Al-Mg alloy for plates, and 6082 type Al-Mg-Si alloy for extrusions [10]. These alloys were found to be reliable in marine service as well as during manufacturing. The specific properties needed for marine applications are related to the specific alloy conditions. In respect to the Al-Mg alloys with Mg content $\geq 3\%$ wt., the Aluminum Association received the H116 and H321 tempers [15]. The H116 products are strain hardened at the last operation in the processing schedule, while the H321 is thermally stabilized. In both procedures the same level of mechanical properties is achieved, meeting the specified levels of corrosion resistance which is assessed in accelerated corrosion tests (NAMLT and ASSET), regarding inter-granular and exfoliation types of corrosion. These H116/H321 tempers of marine grade alloys are suitable for continuous service at temperatures $< 66^{\circ}\text{C}$. Previously, the H116 temper required only exfoliation testing while the H321 temper had no defined requirement for corrosion testing. Those new H116 and H321 tempers are specified in the recently established ASTM B928 standard for "High Magnesium Aluminum Alloy Sheet & Plate for Marine Service".

The heat-treatable 6082 alloy extrusions are usually specified for the marine market as T6 temper, which can be attained after solution heat-treatment and artificial aging.

The demand for new materials with improved properties was targeted toward the development of new alloys or improvement of the basic types with the idea to increase the strength either before or after welding which is of the up most importance. Increased after-welding strength can be achieved by modifying either the plate, or extrusion material, or filler wire. The welding improvement is essential in improving the fatigue behavior also. The general need for enhance the strength parameters should be always followed by preservation of the excellent corrosion resistance or formability behavior of the basic 5083 or 6082 alloys.

The most attractive improvement was achieved by Pechiney Marine Group in 1995 [11], after a small chemistry modifications of the 5083 alloy. The new alloy was designed as 5383. Compared to 5083, the 5383 alloy is characterized by: (i) lower Si and Fe maximum allowable contents;

Table 3. *Chemistries of aluminum alloys for marine applications*

Alloy	%	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr	Al
5083	min				0.40	4.0	0.05				rest
	max	0.40	0.40	0.10	1.0	4.9	0.25	0.25	0.15		
5383	min				0.7	4.0					rest
	max	0.25	0.25	0.20	1.0	5.2	0.25	0.40	0.15	0.20	
5383NG	min				0.8	4.3				0.05	rest
	max	0.25	0.25	0.10	1.1	5.3	0.15	0.40	0.15	0.20	
5059 "Alustar"	min				0.6	5.0		0.40		0.05	rest
	max	0.45	0.50	0.25	1.2	6.0	0.25	0.9	0.20	0.25	
5086	min				0.20	3.5	0.05				rest
	max	0.40	0.50	0.10	0.7	4.5	0.25	0.25	0.15		
5754	min					2.6					rest
	max	0.40	0.40	0.10	0.5	3.6	0.3	0.20	0.15		
5052	min					2.2	0.15				rest
	max	0.25	0.4	0.1	0.1	2.8	0.35	0.1	/		
5454	min				0.5	2.4	0.05				rest
	max	0.25	0.4	0.1	1.0	3.0	0.2	0.25	0.2		
5456	min				0.5	4.7	0.05				rest
	max	0.25	0.4	0.1	1.0	5.5	0.2	0.25	0.2		

(ii) Higher Mn minimum allowable content; (iii) Higher Cu, Mg, Zn and Zr maximum allowable contents. The listed differences brought an advantage as a ~ 15% higher welded strength (Table 2, Fig.1), increased fatigue strength (Table 4), as well as a better corrosion resistance [11]. The formability behavior is preserved at the same level as it is for the basic 5083 alloy type.

Table 4. Fatigue strength of welded 6 mm thick H116 plates [10]

Alloy	Thickness (mm)	Filler wire	Fatigue strength at 10 ⁷ cycles (weld beam on) (MPa)
5083	6	5183	148
5383	6	5183	167

Additional chemistry tuning, allowing higher Mg and Mn ranges, lower Cr and Cu maximum level and a slightly higher Zr content, leads to the upgraded 5383 alloy - marked as 5383 NG [13]. This change was followed by further increase of the after welding yield stress (YS). The comparison of the basic mechanical properties shown in Fig.1 clearly reveals that the minimum after welding YS of the 5083 alloy was increased from 125 MPa to 145 MPa by introducing the 5383 type alloy, and finally the 5383 NG type offers the after welding YS of 160 MPa.

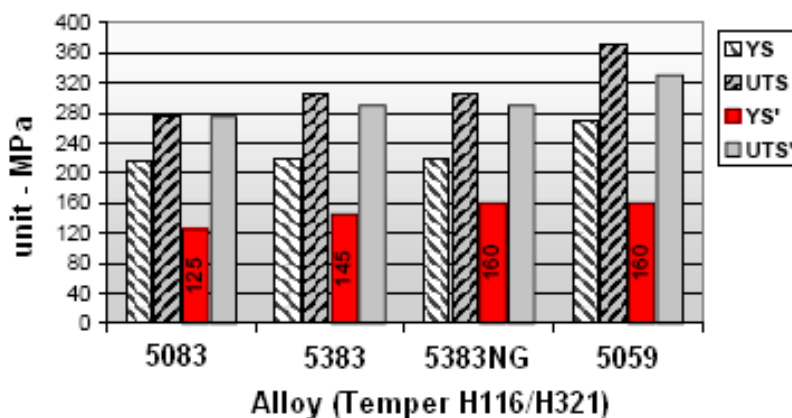


Fig.1. Minimum mechanical properties of 5083, 5383 and 5059 alloy types [13].

Similar after welding strength was achieved by the recently developed 5059 ("Alustar") alloy type [14], with a somewhat higher copper content (Table 3). This alloy seems to have also a higher fatigue resistance than the 5083 type alloy.

The Pechiney Marine Group and Nigel Gee and Associates LTD reported an interesting analysis [12] showing that the 6082 T6 extrusion replacement with 5383 H112 grade extrusions in the ship constructions with 5383 H116 plates brought an additional average weight saving of about 5%. This saving was not followed with any production cost increase.

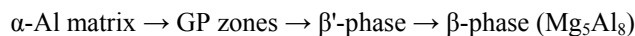
Corrosion control and processing of Al-Mg alloy plates

High content of Mg (from 4-6 wt.%), provides good strength level of standard 5083 and new developed 5383, 5383NG and 5059 Al-Mg alloys for marine application [13,14]. On the other hand, benefit of increasing the strength with increasing the Mg content is followed by decreasing of corrosion resistance, due to the tendency of Mg atoms to be precipitated as highly anodic β -phase (Mg_5Al_8) particles, preferably distributed along grain boundaries. In order to find out a balance between mechanical

properties and corrosion resistance, an optimization of chemical composition and microstructure development during thermomechanical treatment (TMT) is necessary to be achieved.

Corrosion behavior.

In Al-Mg alloys with high Mg content ($>3\%$ Mg) solid solution is supersaturated with Mg solute atoms, because the Mg content is higher than $1,9\%$ Mg, which is the equilibrium solubility of Mg in Al-matrix at room temperature [16]. In that case, Mg solute atoms tend to precipitate out as an equilibrium β -phase (Mg_5Al_8) along the grain boundaries or randomly distributed in the structure. Precipitation sequences of the decomposition of supersaturated solid solution have been reported earlier [17] as follows:



This process occurs slowly even at room temperature, and could be significantly accelerated at high temperatures ($>65^\circ\text{C}$). Since the corrosion potential of β -phase ($-1,24\text{V}$), is more negative than the potential of Al-matrix ($-0,87\text{V}$), dissolution of anodic β -phase particles would occur in an appropriate solution, such as seawater [18]. This corrosion process is schematically illustrated in Fig.2. Other second phase particles, such as $MnAl_6$, have no influence on the corrosion behavior of Al-Mg alloys, since the corrosion potential of $MnAl_6$ particles ($-0,85\text{V}$) is as much as the potential of Al-matrix.

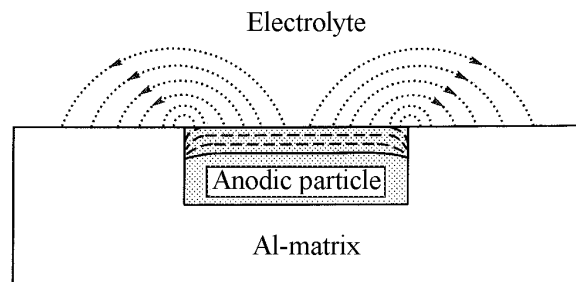


Fig.2. Schematic illustration of corrosion process at the interface between anodic particle and corrosion solution [19].

The susceptibility of Al-Mg alloys to different forms of corrosion (intergranular, stress corrosion and exfoliation) depends not only on the presence of β -phase particles, but mostly on its form and distribution in the structure. Figs.3 and 4 [18,20] show different microstructures with β -phase precipitated as a continuous layer along grain boundaries in 5356 Al-Mg alloy (Fig.3b,c), or at shear bands in deformed 5083 Al-Mg alloy (Fig.4), while Fig.3a,d show random distribution of β -phase precipitated out in a globular form within the structure. Microstructures with continuous layer of β -phase (Fig.3b and Fig. 4) are highly susceptible to corrosion, while randomly distributed β -phase in the structure (Fig.3a,d) provides high corrosion resistance of 5083 Al-Mg alloy. Fig.3c shows the microstructure slightly susceptible to corrosion since β -phase is partly present in a globular form.

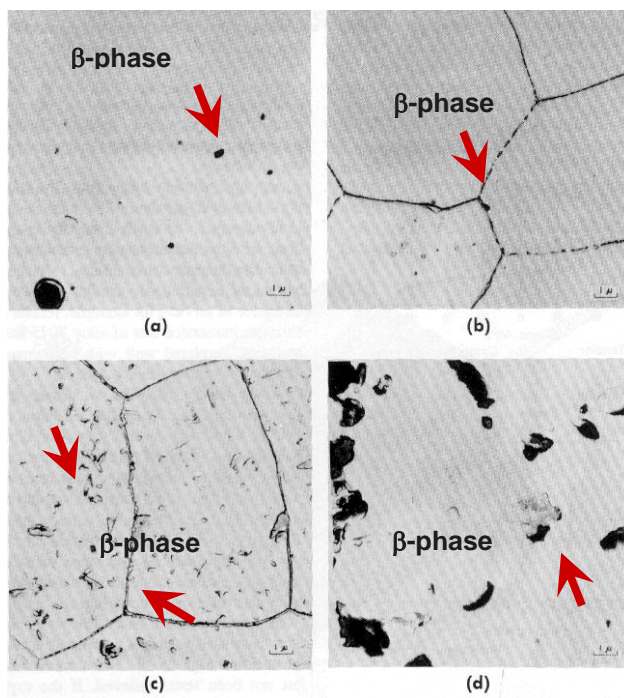


Fig.3 Microstructures of Al-Mg alloy 5356-H12 with varying degrees of susceptibility to stress corrosion cracking (SCC): a,d) highly resistant; b) highly susceptible; c) slightly susceptible [18].

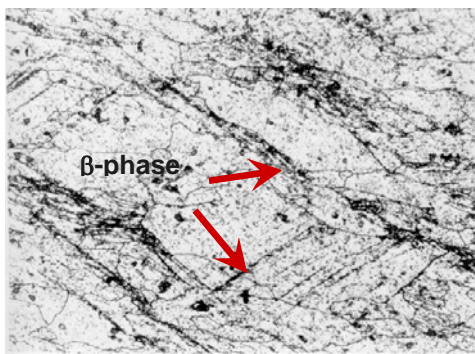


Fig.4 Microstructure of Al-Mg alloy 5083 after deformation and heating at 120°C/24h, highly susceptible to SCC [20].

Basic forms of corrosion

The most important corrosion processes in Al-Mg alloys are: intergranular corrosion (IGC), stress corrosion cracking (SCC) and exfoliation [18]. These forms of corrosion are strongly dependent on the microstructure developed during TMT. *Intergranular and stress corrosion* occur along electrochemically active path in grain

boundary region, where a localized decomposition of solid solution, or anodic β -phase particles are present. Intergranular corrosion has been experienced in Al-Mg-Si and Al-Mg alloys with $>3\%$ Mg. For the stress corrosion occurrence, three factors are necessary: tensile stress, corrosion environment and susceptible metallurgical structure. This type of corrosion has been observed in high-strength Al-Zn-Mg alloys and Al-Mg alloys with $>3\%$ Mg. Al-Mg-Si and Al-Mg alloys ($<3\%$ Mg) are not susceptible to SCC. *Exfoliation* is a lamellar form of corrosion that occurs also along grain boundaries, parallel to the metal surface. Microstructure susceptible to exfoliation is characterized by elongated grains produced by cold working and by a presence of continuous layer of grain boundary precipitates.

Corrosion Testing [4,18]

The susceptibility to IGC of Al-Mg alloys can be determined using NAMLT test (Nitric Acid Mass Loss Test) which is described in ASTM G67 standard [4]. It consists on the immersion of the tested specimen in concentrated HNO_3 at 30°C for 24h, and measuring the mass loss. Specimens susceptible to IGC lose 25-75 mg/cm^2 , while the specimens resistant to IGC lose between 1-15 mg/cm^2 .

The susceptibility to exfoliation can be determined by visual inspection using ASSET method (Method for Visual Assessment of Exfoliation Corrosion Susceptibility of AA5xxx Series Al alloys), which is described in ASTM G66 standard [4]. It consists on the immersion of specimens in an appropriate solution at 65°C for 24h.

In order to examine SCC susceptibility, slow strain rate testing (SSRT) is recommended to be used, and it is described in ASTM G129 standard [4] (Standard Practice for SSRT to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking). It consists on the slow strain rate tension test in the corrosive environment. For the assessment of SCC susceptibility, total elongations are measured, and compared with those in slow rate tension in dry air.

Corrosion prevention methods

The manufacturing process of the marine grade Al-Mg alloys needs a careful control, in order to ensure proper structure refinement, starting even in the hot rolling sequence. During the cold rolling and subsequent annealing, final structure tuning should be done. The basic request in manufacturing practice of Al-Mg alloys with $>3\%$ Mg for marine application, is related to the control of the precipitation of β -phase (form and distribution), which could be highly sensitive to the seawater attack. The continuous precipitation of β -phase along the grain boundary should be avoided as well as the pancake structure and segregations from cast structure. Discontinuous β -phase precipitation and equiaxed grain structure reduce the susceptibility to grain boundary or intergranular corrosion and exfoliation, respectively.

Different tempers of highly alloyed Al-Mg alloys for marine application, such as H116 and H321, are developed to produce the microstructures with β -phase precipitates within the grains, in order to eliminate corrosion susceptibility. On the other hand, new Al-Mg alloys with small addition of Zn, such as 5383, 5383NG and 5059, have been designed in order to improve corrosion resistance of standard Al-Mg alloys, such as 5083 alloy [13,14]. The role of Zn addition, which preferably precipitates in the form of

Zn-based particles, is to eliminate β -phase precipitation in the form of continuous layer along grain boundaries, and to reduce corrosion susceptibility of Al-Mg alloys as well.

It has been reported earlier [14] that alloy 5059 (containing 0.4-0.9 wt.%Zn) in H116/H321 tempers, has better resistance to intergranular and exfoliation corrosion, which is evaluated by the ASSET and NAMLT tests, than standard 5083 alloy. The test results on the examination of alloy 5383 (containing up to 0.4 wt.%Zn) have shown that corrosion resistance is as good as for standard 5083 alloy [13], while alloy 5383NG (with modified chemistry given in Table 3) has better corrosion properties in comparison with alloys 5083 and 5383. For all the examined alloys (5083, 5383, 5383NG and 5059) the corrosion tests were performed on the samples before and after welding procedure.

Other methods of corrosion prevention

Aluminium anodizing is an electrochemical method of making a protective aluminum oxide film Al_2O_3 , at the surface of Al-alloy products [18]. Cladding is a method of coating of Al-alloys products by thin layer of pure Al or Al-alloys. If the cladding layer is anodic in comparison to the base Al alloy, the products are called alclad products. Alloy 7072 – Al-1Zn is used as cladding for Al-Mg and Al-Mg-Si alloys.

Summary

The prospective of aluminum alloys application, with special task on using of Al-Mg types in the shipbuilding, was considered through property/cost effectiveness.

The total weight saving estimated by over 50% in boats or ships constructions, after introducing aluminum alloy components, makes the aluminum's future in shipbuilding really promising. It seems that the marine application of aluminum alloys nowadays is strongly funded on the benefits as the (i) lightweight; (ii) excellent corrosion resistance; and (iii) low cost maintenance.

In respect to the selection of Al-alloys, the properties/cost effectiveness of Al-Mg alloys recognized through the excellent corrosion resistance, weldability, formability, reliable manufacturing process, and ensuring at least 10% lower production costs in respect to the other suitable Al-alloys, makes them as most attractive for the steel replacement in shipbuilding.

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