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Corrosion behaviour of aluminium alloys in deep-sea environment: A review and the KM3NeT test results

Elisa Canepa[*], Roberto Stifanese, Lorenzo Merotto, Pierluigi Traverso

Institute of Marine Sciences - National Research Council (ISMAR-CNR), Genoa, Italy

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ABSTRACT

The interest in deep-sea environment is increasing both in the scientific and business community. Nevertheless, in situ corrosion studies are difficult to be executed due to high experimental cost and technical problems, consequently they are quite uncommon. After a summary of the scarce available literature about deep-sea environment studies on corrosion of aluminium alloys, results of an in situ exposure of Al 5083 H111, Al 6082 T6, Al 7075 T651, Al 8090 T81 alloys are presented. Specimens were exposed for 6, 12, and 18 months in deep-sea, at a depth of approximately 3350 *m*, off the Capo Passero (Sicily, Italy) in the KM3NeT project framework. Corrosion attack was evaluated by gravimetric weight loss measurements. Localised corrosion was investigated by using a digital camera and ImageJ software in addition to different microscopic techniques to better identify morphological/chemical details. Al 7075 T651 and Al 8090 T81 alloys performed much worse than Al 5083 H111 and Al 6082 T6 alloys. Al 6082 T6 alloy was the most resistant to corrosion, while Al 8090 T81 suffered the most relevant damage. Both Al 5083 H111 and Al 6082 T6 did not show any significant visible corrosion attack, while both Al 7075 T651 and Al 8090 T81 suffered severe localised attack. Al 8090 T81 experienced mainly pitting corrosion, while Al 7075 T651 was seriously affected by pitting, crevice, and exfoliation. The microstructural heterogeneity of both Al 7075 T651 and Al 8090 T81 alloys increases susceptibility to localised corrosion attack thus discouraging any deep-sea use of these alloys.

1. Introduction

Currently, more and more effort is being devoted to both scientific exploration and resource exploitation of deep-sea. This extreme environment is characterized by total absence of sunlight, high hydrostatic pressure (it increases 1 atm for each 10 *m* in depth), and a low water temperature of about 3 °C (apart from hydrothermal vent fields where the temperature of water that emerges from the chimneys may be as high as 400 °C). Full-depth monitoring is needed to better understand climate processes that control ocean warming and to envisage its trend in upcoming decades. Challenging scientific research is trying to advance the understanding of the deep-sea environment, and its innovation potential is highlighted by virtue of more and more advanced technical tools, (e.g. [1–3]). In parallel, even if a precautionary approach is recommended [4], research directed towards the commercial feasibility of deep-sea resource exploitation is increasing even more to search for oil, gas and minerals (e.g. [5–7]).

The aluminium alloys are used in marine environments, even if their application requires expert advice [8]. In general, aluminium is attractive because of it is a light metal and can be obtained with high strengths [9]. Aluminium alloys have excellent corrosion resistance to a wide variety of exposure conditions [10–12]. Other aluminium properties are attractive for specific uses, for instance:

* Corresponding author. Institute of Marine Sciences - National Research Council (ISMAR-CNR), Via De Marini 6, I-16149, Genova, Italy.
E-mail address: elisa.canepa@ismar.cnr.it (E. Canepa).

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electrical and thermal conductivity, good formability, corrosion resistance, light and heat reflectivity, nonmagnetic behaviour, and recyclability [9]. The resistance of aluminium to corrosion is due to a film of aluminium oxide that forms on its surface [13–15]. The usual passive film that forms on aluminium immersed in water at temperatures below 70 °C is bayerite [16]. In seawater, this naturally formed protection film breaks down more promptly and its repair is retarded by the chloride ion [e.g., [17]]. Deep-sea lower dissolved oxygen and higher salinity with respect to shallow water facilitate further aluminium alloys corrosion [18]. In addition, the deep ocean environmental zone is generally undersaturated in carbonates, which reduces the likelihood of forming protective calcareous layers [19]. The corrosion in seawater is usually of the pitting and crevice types. Low weight losses and low corrosion rates characterize these manifestations of localised corrosions. Therefore, the integrity of an aluminium alloy structure needs to be evaluated on the basis of measured depths of pits and crevice corrosion instead of corrosion rates calculated from weight losses.

As early as the 80s and the 90s Beccaria and co-workers performed a number of laboratory experiments to study the effects of high hydrostatic pressure on corrosion of aluminium alloys in natural seawater [20–22]. The results of these experiments demonstrated that hydrostatic pressure is a crucial aspect to take into account, and a number of high hydrostatic pressure laboratory experiments simulating deep-sea environment were also carried out more recently (e.g. [23]).

Although the results of laboratory experiments, which are performed under controlled conditions, may be useful to investigate fundamental corrosion mechanisms, they may not relate well to natural environment [8,24]. Deep-sea is a complex system, in addition to hydrostatic pressure, other factors influence corrosion: temperature, dissolved oxygen, salinity, pH, seawater current, suspended silt, marine biota, decaying organic material, dissolved sulphides and carbonates, etc. (e.g. [25]). To determine in situ deep-sea corrosion behaviour, environmental variables must be considered as a whole because of their interrelated impacts [26,27]. Specific in situ studies have to be performed in order to obtain comprehensive information about corrosion of materials in deep-sea environment. However, these studies are difficult to be executed due to high experimental cost and technical challenges and they are quite uncommon in the available literature [28].

The KM3NeT (Cubic Kilometre Neutrino Telescope - http://www.km3net.org; accessed November 8, 2017) deep-sea corrosion experiment is one of these rare studies. Aluminium, copper, and iron alloy specimens were exposed in the Western Ionian Sea, off Eastern Sicily, Italy, at a depth of about 3350 *m*, in the framework of the design of the KM3NeT research facility for detection of Extreme High energy neutrinos - an instrument that aims to exploit several cubic kilometres of the deep Mediterranean sea as its detector medium. The main aim of this deep-sea exposure experiment was to provide information about corrosion of materials considered to design the submerged telescope tower infrastructure [29], but the study of some of them (e.g., Al 8090 T81) was curiosity-driven.

The present paper is focused on the corrosion behaviour of aluminium alloys in deep-sea. It gives an overview on the scarce available literature about in situ deep-sea studies on corrosion of aluminium alloys (Section 2) and it outlines results from the KM3NeT deep-sea corrosion test. Section 3 describes the KM3NeT deep-sea corrosion experimental setup, and Section 4 the analysis methodology of the aluminium alloys. Section 5 deals with presentation and discussion of results, while conclusions are summarized in Section 6.

2. A review about in situ deep-sea environment corrosion studies of aluminium alloys

To our knowledge, only six publications - [18,30–33], and [34] in Chinese - deal specifically with in situ deep-sea experiments on corrosion of aluminium alloys. In addition, Bellou et al. [35] concerns a deep-sea experiment about microbial communities developed on different substrata among which aluminium.

Reinhart [18] presents the performance data of the comprehensive program initiated in 1960 by the Civil Engineering Laboratory - Naval Construction Battalion Center (NCEL), Port Hueneme, California, to obtain information on the behaviour of construction materials in deep-sea environments. Approximately 20000 specimens of about 475 different materials were exposed between 1962 and 1970 at two site in the Pacific Ocean, approximately 81 nautical miles southwest and 75 nautical miles west of Port Hueneme, at nominal depths of 2500 and 6000 feet (762 and 1829 *m*, respectively) for periods of time varying from 123 to 1064 days. At a third site, they were exposed at the surface for comparison purposes. The test specimens included steels, cast irons, stainless steels, copper, nickel, aluminium, miscellaneous alloys, and wire ropes. In particular, 1000, 2000, 3000, 5000, 6000, 7000 series of aluminium alloys were investigated. The 7000 series alloys behaved in an erratic manner, it was impossible to find any correlation between their corrosion behaviour and duration of exposure, effect of depth, or the effect of changes in the concentration of oxygen in seawater. The 1000, 2000, 3000, 5000 series of aluminium alloys showed an erratic behaviour due to changes in concentration of oxygen. While the corrosion rates and maximum depths of pitting and crevice corrosion of alloy 6061 - the only one 6000 series alloy tested - decreased with increasing concentration of oxygen in seawater. All series showed erratic behaviour with respect to duration of exposure. On the contrary, a clear depth-dependent trend was outlined: corrosion rate increased with increasing seawater depth and the typical pitting and crevice corrosion were more severe in deep water than at the surface. For example, 6061-T6 alloy after about 400 days of immersion showed a maximum pit depth of about 0.4 mm and 1.5 mm at a depth of about 1.5 *m* and 2050 *m*, respectively. No crevice was detected in the shallow water test, while the crevice depth was about 1.4 mm in deep water. Therefore, contrary to other materials, for which the effects of depth were either negligible or in the sense of reducing the consumption rates, aluminium alloys, in general, were detrimentally affected.

Around the same time, from April 1968 to August 1972 precisely, Lockheed Missiles and Space Company, Sunnyvale, California, performed deep-sea corrosion tests to evaluate the effectiveness of seven protective paint coating systems on aluminium alloys and both structural and stainless steels [30]. Corrosion test specimens were placed both in the Atlantic Ocean on the bottom of the Tongue