Ocean Engineering 87 (2014) 10–15

Contents lists available at ScienceDirect

Ocean Engineering

journal homepage: www.elsevier.com/locate/oceaneng

Short Communication

A review of studies on corrosion of metals and alloys in deep-sea environment

Pierluigi Traverso, Elisa Canepa*

National Research Council of Italy – Institute of Marine Sciences (CNR-ISMAR), Via De Marini 6, I-16149 Genoa, Italy

ARTICLE INFO

Article history:
Received 10 July 2013
Accepted 16 May 2014
Available online 11 June 2014

Keywords:
Deep-sea
Corrosion
Metals
Alloys
Shipwrecks

ABSTRACT

The interest in deep-sea environment is increasing both in the scientific and business community. In order to meet deep-sea challenges great performances for structure materials are requested, but in situ studies are difficult to be executed due to high experimental cost and technical problems. Indeed, they are quite uncommon in the available literature compared with the amount of research in shallow sea water. This paper reviews the scarce available literature about deep-sea environment studies on corrosion of metals and alloys, some outlines of investigations on sunk objects are given.

1. Introduction

The deep-sea environment is very different from the sea at the surface. It 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 – as it emerges from the chimneys – may be as high as 400 °C. Despite these severe conditions, more and more effort is being devoted to both scientific exploration and resource exploitation of the deep-sea environment.

On the one hand, challenging scientific research is trying to advance the understanding of the deep-sea environment and to highlight its innovation potential. More and more advanced technical tools (e.g., Fletcher et al., 2009; Zhang et al., 2012) can be applied to frontier topics. The ability to survey the sea floor chemical conditions associated with potential sub-sea geologic CO_2 disposal in abandoned oil/gas fields, and the detection of the structure and composition of complex gas hydrates to try to define both their potential as energy resource and their role in the global carbon cycle (Milkov, 2004) are just a couple of examples. On the other hand, research directed towards the commercial feasibility of deep-sea resource exploitation is increasing to search for oil, gas and minerals (e.g., Kato et al., 2011), even if concerns can arise (Van Dover, 2011) about conservation of special habitats in the deep-sea (as an example, the hydrothermal-vent stalked barnacle *Vulcanolepas osheai* is shown in Fig. 1). Therefore, both the scientific and business community increasingly request great performances for structure materials – like metals and alloys – in deep-sea environment.

Laboratory experiments that are performed under controlled conditions are used to investigate deep- sea corrosion behavior of materials, which are expected to be subject to different physical-chemical environmental condition with respect to the near surface sea. We just cite some examples in which individual effects of deep-sea environment on corrosion of metals and alloys were investigated by laboratory simulations.

Beccaria and co-workers (Mor and Beccaria, 1978; Beccaria and Poggi, 1985, 1986; Beccaria et al., 1989, 1991, 1993, 1994, 1995) were very active in the field of the laboratory experiments to study the effects of high hydrostatic pressure on corrosion of metals and alloys. Among other investigations, they studied the effect of hydrostatic pressure on corrosion of both aluminum and 6061-T6 aluminum alloy in sea water. This study evidenced that corrosion of aluminum increased on increasing the hydrostatic pressure, in prevalence as an effect of increasing in localized corrosion; deeper pits were formed on 6061-T6 aluminum alloy as well, but generalized corrosion of this alloy decreased due to the formation of Mg–Al oxide layer, which was more protective than aluminum hydroxides.

More recently, in their laboratory studies Zhang et al. (2009), Yang et al. (2010), and Liu et al. (2012) investigated the effect of hydrostatic pressure in NaCl solution on the corrosion behavior of Fe–20Cr alloy, Ni–Cr–Mo–V high strength steel, and nickel, respectively. They investigated in the details pit corrosion mechanism and they found that the corrosion susceptibility was increased in the presence of higher hydrostatic pressure. In a further study

---

* Corresponding author. Tel.: +39 010 6475 403; fax: +39 010 6475 400.
E-mail address: elisa.canepa@ismar.cnr.it (E. Canepa).

http://dx.doi.org/10.1016/j.oceaneng.2014.05.003
0029-8018/

Fig. 1. The stalked barnacle, *Vulcanolepas osheai*, at a depth of 2628 m on the side of a "cool" chimney at the Kilo Moana vent field on the Northern Eastern Lau Spreading Center. Picture by Professor Charles Fisher. Courtesy of Marine Geoscience Data System (MGDS; www.marine-geo.org).

about Ni–Cr–Mo–V high strength steel, Yang et al. (2013) found that with the increase of hydrostatic pressure, the pit growth rate parallel to steel surface increased and the coalescence rate of neighboring pits was promoted. Therefore, it took shorter time to complete the evolution from wide-shallow shape pits to uniform corrosion as a result of the interaction between electrochemical corrosion and elastic stress. Lastly, we mention the Sun et al. (2013) paper about corrosion behavior and efficiency drop of Al–Zn–In–Mg–Ti sacrificial anode in simulated deep water environment.

But the materials tested in laboratory conditions may behave in unexpected manner in natural environment (Sawant et al., 1993; Hartt 2012). In fact, deep-sea is a complex system: local values of hydrostatic pressure, temperature, dissolved oxygen (DO), salinity and pH (e.g. see Dexter and Culberson, 1980), in addition to other factors – like sea water current, suspended silt, marine biota, decaying organic material, dissolved sulfides and carbonates – determine the result of in situ marine corrosion experiments. These environmental variables must be considered not singly, but as a whole because of counterbalancing actions (Bombara et al., 1986a) and the effect of each of the factors affecting corrosion behavior is not readily distinguishable (Venkatesan et al., 2002). It is not possible to duplicate all the in situ deep-sea variables and the changes in these variables that prevail in any one environment or location (Reinhart, 1976). Therefore, in situ deep-sea studies are relevant in order to obtain comprehensive information about metal and alloy corrosion in deep-sea environment. Despite of this, these studies on materials are difficult to be executed due to high experimental cost and technical challenges. Indeed, they are quite uncommon in the available literature compared with the amount of research in shallow sea water.

This review intended to give a brief overview of the scarce available literature about in situ deep-sea studies on corrosion of metals and alloys, and some outlines about investigations on sunk objects. For a more engineering-oriented review see Bombara et al. (1986a,1986b). Relevant information about the topic can also be retrieved from Heiser and Soo (1995). Furthermore, we point out the reviews of Fassin and Traverso (2008, in Italian) and Zhou et al. (2010, in Chinese).

2. A literature overview about in situ deep-sea environment corrosion studies

Since there was very little published information on the behavior of construction materials in deep-sea environments, an extensive program was initiated in 1960 by the Civil Engineering Laboratory – Naval Construction Battalion Center (NCEL), Port Hueneme, California, to obtain such information (Reinhart, 1976). Between 1962 and 1970 approximately 20000 specimens of about 475 different alloys were exposed at two sites in the Pacific Ocean, approximately 81 nautical miles southwest and 75 nautical miles west of Port Hueneme. The test specimens included steels, cast irons, stainless steels, copper, nickel, aluminum, miscellaneous alloys, and wire ropes. These specimens were exposed at nominal depths of 2500 and 6000 ft (762 and 1829 m, respectively) for periods of time varying from 123 to 1064 days and at the surface, at a third site, for comparison purposes. It is not possible to adequately summarize the huge amount of detailed information provided by the Reinhart (1976) report, but just to round up main results about general corrosion, the effects of depth were either negligible or in the sense of reducing the consumption rates, exception made for aluminum alloys, which were detrimentally affected. The typical pitting and crevice corrosion of aluminum in seawater were more severe at depth 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.

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 aluminum alloys and both structural and stainless steels (Rynewicz, 1974). Corrosion test specimens were placed both on the Naval Applied Science Laboratory's Deep Ocean Material Array, which at that time was about to be installed on the bottom of the Tongue of the Ocean (Atlantic Ocean) at 4050 ft (1234 m), and on a NCEL Deep Ocean Material Array in the Pacific Ocean at 5900 ft (1798 m). The Pacific specimens were exposed for six months, while the Atlantic ones for more than four years. As an example, comparing results for uncoated stainless steels, the two site specimens maximum crevice corrosion was about 2.5 mm versus about 3.0 mm, respectively. To explain this limited difference, Rynewicz affirmed that the Pacific site with its very low oxygen content ($1.6\,\mathrm{ml\,l^{-1}}$) initiated loss of passivity (at local crevices) much more rapidly than the higher oxygen content test site in the Atlantic ($5.7\,\mathrm{ml\,l^{-1}}$). As a general conclusion of his paper, Rynewicz stated that four epoxy coating systems provided very good to excellent protection.

In the Seventies, the Institute of Oceanology of the Academy of Science of the USSR was active in deep-sea corrosion test studies as well (Ulanovskii and Egorova, 1978; Ulanovskii, 1979). Corrosion of carbon steel, stainless steel, copper, brass, and aluminum alloys was investigated performing experiments lasting 20, 40, and 70 days in the northwest sector of the Pacific Ocean and in the Sargasso Sea. From their data, they concluded that hydrostatic pressure did not greatly influence corrosion of the tested metals, but they suggested temperature influence – see also the investigation about such data performed by Melchers (2005). In principle, results from Reinhart (1976) were confirmed. We believe that major differences concerning the behavior of aluminum alloys are