

CORROSION AND METAL PROTECTION IN SEAWATER

Boris B. Chernov

The article deals with the evolutionary models of the corrosion mechanisms and metals protection in seawater. It is shown that the best model to describe the experimental data is the one that takes into account the presence of the biofilm on destroying metal surfaces.

Keywords: sea water corrosion, metals protection, marine corrosion, mechanism of corrosion, biological corrosion, biofilm, corrosion prediction.

Most metal-consuming structures for use in sea water (ships, oil platforms, piers, pipelines, etc.) are traditionally made of mild low-carbon and low-alloy steels and without special protection are under considerable corrosion wear. To date, there is the certain progress in understanding of physical-chemical effect of metals crumbling process in seawater, depending on its characteristics. Based on these concepts it is possible to implement practical ways to reduce corrosion losses or complete prevention of corrosion. The purpose of this article is the consideration of the dynamics in the study of corrosion processes and protection of metals in sea water in terms of development prospects for this field of knowledge.

Seawater metal corrosion mechanism

All theoretical views on the nature and mechanism of metals destruction in sea water are based on a large number of experimental data obtained due to direct corrosion tests or operation experience of different facilities in different years by different researchers. Of course, those views absorbed and followed all the achievements of basic sciences in physical chemistry, electrochemistry and chemistry of solids. With the development of views on the mechanism of metal corrosion it is possible to distinguish several stages of evolutionary ideas about sea water corrosiveness and seawater metals corrosion behavior.

1. Multiple recording of experimental evidences of seawater significant corrosiveness is explained by the presence of high concentrations of chloride ions in seawater. Those ions cannot allow forming durable protective corrosion products at the metal-seawater boundary. To date, large amount of information about most metals and their alloys corrosion behavior is accumulated, but unfortunately, often it is not available due to institutional barriers. Moreover this information is highly fragmented and often does not include details about corrosion tests, without which is difficult to judge about the laws and regularities of the corrosion process. Understanding of inferiority of separate corrosion tests led the researchers to large international projects with long periods of testing and seawater characteristics control at test spots [1,2]. Unfortunately, until now there is no a marine corrosion databank with free access of interested scientists. This makes the researchers to use their own databases which may be in contradiction to each other.

2. Both single and group corrosion tests were showing a permanent downward tendency of the corrosion rate due to time of metal stay in seawater.

3. This dependence is explained by a majority of specialists that corrosion products generated on the corroding metal slow down supply of the cathode depolarizer (oxygen, soluble in seawater) to the metal surface, which leads to slower rate of metal destruction. When corrosion products go to some fixed effective thickness determined by equal rates of their formation and destruction, corroding metal gains the fixed rate of destruction [3,4].

4. In the corrosion products analysis it is repeatedly recorded the presence of compounds consisting of the crumbling metal itself and the components in seawater. These facts together with development of electrochemistry section about concentration changes around the electrodes allowed to explain appearance of the seawater components in corrosion products and created prerequisites for assessing the contribution to corrosion of various sea water chemical parameters [5,6].

5. Measured concentration changes in seawater near the surface of corrosive metal allow demonstrating that the maximum corrosion rate is determined by the limiting discharge current level of dissolved oxygen, which depends on the concentration of dissolved oxygen in seawater, seawater temperature and speed of water motion [7]. Observation of the concentration changes at the surface of the crumbling metal allows understanding the reasons for inclusion of the seawater components in the metal corrosion products and shows that the solubility product of hydroxides and carbonates of corroding metal is almost always achievable in the real rates of metals corrosion [8].

6. Next natural step in understanding of the metal corrosion kinetics and explaining of quantitative relationships in reducing the rate of corrosion was the researches of kinetics of the corrosion products formation process. Unfortunately, we investigated only simple dependences of the cathode process products crystallization [9]. This can be explained by insufficient study of the mass crystallization processes in the physical chemistry itself. Until it reaches a new level of understanding of the processes of mass crystallization on heterogeneous substrates, it is not worth to expect more advanced models in the kinetics of metals corrosion products formation. Therefore we have to content with approximate models, defining them in physical and chemical characteristics of the products formed from the experimental corrosion tests [10].

7. Today, this dependence can help in calculation of corrosion losses by a certain date of operation and stationary rate of products corrosion [11].

8. Fine statistical analysis of the seawater corrosion test results [12-14] has recently allowed Australian scientists R.Melchers to notice and explain a new regularity in the metal destruction kinetics associated

with the characteristics of seawater as a biological system. As result of the data about the dependences of corrosion losses on the exposure time of the metals in seawater, beyond a period of 0.5 – 1.5 years, it was observed that slow corrosion rate changed to its further growth. This regularity, which is difficult to identify in direct experiments, allows R.Melchers to suggest a fundamentally new model of corrosion in seawater. He has explained the observed transitional period as appearance at the boundary between corroding metal and forming products of specific conditions stimulating life of anaerobic bacteria, metabolic products of which increasing the rate of corrosion [12-16].

9. Such theoretical views fully correspond with new forms of symbiotic co-existence between anaerobes and aerobes, which are called biofilms in Microbiology. We examined such model ideas about possible mechanism of the biofilm formation in [17] without presence of the substrate corrosion products. In this article it is shown that the creation of anoxic zones at the metal surface does not require the development of strong and thick biofilm. Co-existence of aerobes and anaerobes is possible even in well-aerated environments.

Taking into account the contribution of biological factors, such transition to the new model concepts requires reconsideration of our views about the seawater metal corrosion mechanisms and offering fundamentally new ways to protect metals in sea water based on new concepts and provisions.

Methods of metals protection

Considering modern views that biological factors do not change electrochemical nature of metal destruction in seawaters but just alter the concentration of substances at the surface of the crumbling metal due to bacterial metabolism, we can use traditional electrochemical protection of metals. The essence of the electrochemical protection consists in shift of corroding metal potential to negative side. There are two practical ways to implement it. First method so called “cathode protection” implies that shift of the potential of the protecting structures is made by an external DC source.

In second method called “sacrificial protection” the shift of the potential is provided by attaching another metal with more negative potential to the protected metal structure. These low-alloy steels for “sacrificial protection” may be zinc, magnesium, calcium, aluminum and their alloys. Practical implementation of electrochemical protection in fact comes to provide uniform distribution of protective potential at the surface of the complex geometry protected objects; to save electricity by switching off periodically the cathode protection; to select the protectors with the best energy characteristics, current output, anode disintegration and sub-layer destruction performances.

Unfortunately, accumulated over many years experience of electrochemical protection application in real objects is gradually losing because the leading companies, such as “Prometheus” and “CNIIMF” (NSRIC), have lost or continue to lose skilled personnel. This situation is explained by the fact that, as a rule, for practical implementation of the protection of the structures really bringing into service the foreign specialists with their methods, techniques and equipment are often invited. Domestic researchers despite the achievements in corrosion protection field that are often ahead of foreign developments and researches in the same area remain unclaimed in the labor market and lose their skills and professionalism. To confirm this, it is enough to note the adjustable sacrificial protection system on hydrofoil vessels, which, as we know, has not been applied abroad. Our country is, in fact, deprived of the opportunity to participate in the protection of metal-intensive designs and has to relay metal objects security under control of foreign companies.

Another traditional way of metal protection from seawater corrosion is application of coating materials, the number of which is being increased continuously. Currently, producers of paint-and-lacquer materials guarantee its protective properties for over 15 years. Until now the issue of price reduction for pre-painting preparatory works has not been solved yet [18].

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