Micro-Characterization Of Pure Mg And AZ91D Used As Sacrificial Anodes In Reinforced Cement Concrete

Yogesh Iyer Murthy*, Sumit Gandhi , Abhishek Kumar,

Abstract: Off-shore reinforced cement concrete structures are exposed to severe chloride atmosphere and are hence prone to corrosion. Prevention of corrosion of such structures by cathodic protection technique has evolved as a major method. Magnesium and its alloys are very commonly used as sacrificial anodes in this regard. The current paper investigates the micro-characterization of pure Magnesium (Mg) and AZ91D anodes used for cathodic protection of structural steel reinforcement in concrete slabs using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) after 270 days of embedment in concrete. The presence of inter-mettalics was found to decrease the rate of corrosion in AZ91D compared to pure Mg. Bare steel reinforcements with and without anodes were also tested in severe Chloride atmosphere for weight loss and tensile strength on different days and compared for 80 days. The tensile strengths and weight loss of bare steel reinforcements with anodes were found to be much less affected in chloride atmosphere, as against those without anode, indicating the effectiveness of the latter, although similar values of stresses were found for both Mg and AZ91D. The results of micro characterization, tensile strength and rate of corrosion can be used for optimal selection of anodes for different exposure conditions.

Keywords: AZ91D, micro-characterization, cathodic protection, mechanical properties, steel, corrosion.

1 INTRODUCTION

The prevention of corrosion of steel in RCC structures is a herculean task, especially in marine atmosphere. Corrosion mitigation techniques include use of corrosion resistant steel re-bars [1], stainless steel and galvanized steel, thermosetting polymers [2], laminates and reinforced plastics [3], thermoplastics, non-metals like elastomers, use of inhibitors[4], paints[5,6], epoxy coatings[7], powder coating [8] and cathodic protection, each having inherent advantages and disadvantages. The selection of a suitable method largely depends on the degree of exposure of structure, economics and the discretion of the designer. Among the above mentioned methods of corrosion prevention, cathodic protection (CP) technique is unique as most of the other methods (except application of corrosion resistant steel re-bars and stainless steel and galvanized steel) involve coating of suitable material over the steel and subsequent embedment of steel in concrete. The peeling off such coatings while pouring of concrete is a common phenomenon resulting in the ingress of corrosion. On the other hand, CP involves the installation of suitable electrochemically active electrode as anode as an exterior member, designed for a suitable time period. The application of such anodes as exterior member aids in visual inspection and upon the completion of design period, or otherwise, the anodes can be conveniently replaced. Thus, precise monitoring of reinforcement is enabled.

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The commonly used anodes for CP of steel in concrete are Aluminum, Magnesium and Zinc anodes, in either pure form or as alloys in varying proportion [9]. The primary objective of the current investigation is thus to experimentally investigate the mechanical properties of steel which is electro-chemically in contact with Mg and AZ91D anodes in high chloride atmosphere, the rate of corrosion of the two anodes and to understand the micro structural features of the corroded anodes after significant days of embedment in concrete containing free chloride ions. The outcome of such experimental investigations is expected to aid in judicious selection of right anodes for excess chloride exposure condition.

2. EXPERIMENTAL SET-UP

The current work is carried out in two stages. A set of experiment is carried out with bare steel reinforcements, while another set of experiments with reinforcements embedded in concrete containing free chloride ions. The experimental set up for both the cases is discussed below.

2.1 Experimental set up for bare steel in chloride atmosphere:
In order to investigate the performance of pure Mg and AZ91D anodes on corrosion prevention of bare steel reinforcements three set of six steel reinforcements were tied together intact with centrally placed anode to complete the electrochemical cell as shown in Fig.1. All the samples were dipped in high chloride atmosphere of 7.5% NaCl in tap water with specifications shown in Table 1. Sample set one did not contain any anode; sample set two consisted of AZ91D anode while sample set three contained pure Mg anode. These samples were tested for weight loss, tensile strength and microstructure.

Table 1 *Tap water characteristics confirming IS: 10500:2012 [10]*

S No.	Parameter	Value
1	Chloride	168mg/l
2	pH	7.6
3	Fluoride	0.4mg/l
4	Dissolved Oxygen	10.15mg/l
5	Chemical Oxygen Demand	0
6	Biological Oxygen Demand	0
7	Free Residual Chlorine	0.1mg/l

2.2 Experimental set-up for embedded steel in concrete:
Reinforced cement concrete slab of dimension 1000mm X1000mm X100mm was cast using 1:1.5:3 nominal mixes and a water to cement ratio of 0.45. Reinforcement mat of 10mm diameter steel was placed with a clear cover of 25mm from sides and top surface of concrete with a center to center spacing of 190mm as shown in Fig.1. The surface area of steel reinforcement mat was found to be 1.884m2. The reinforcements were treated with pickling solution in order to remove corrosion sites. Anodes 22mm diameter and 250mm long were centrally placed and tied intact to complete the electrochemical cell. Two slabs were casted with 3.5% NaCl by weight of cement using pure as cast, Mg anodes and AZ91D anodes respectively. These slabs were constructed using tap water with specifications as shown in Table 1 on the same day, so as to maintain similar casting conditions.

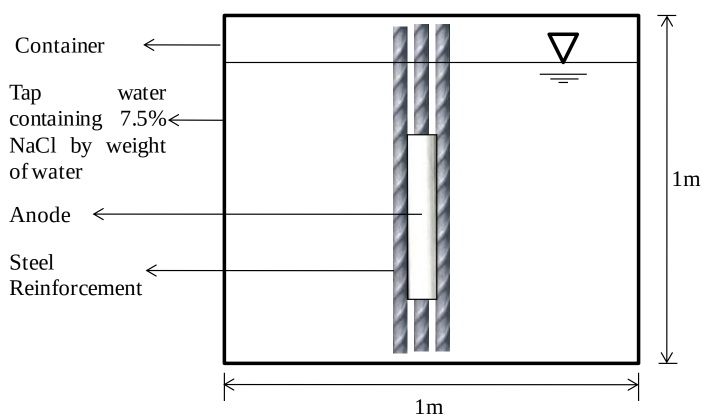

Fig.1 *Schematic of set-up used to access the performance of anodes in high NaCl content atmosphere.*

3. Results and Discussions

The mechanical properties such as, yield stress, ultimate tensile stress and elongation of steel bars were ascertained at different days of immersion in 7.5%NaCl solution and the variation in relevant values were studied. Anodes (both Mg and AZ91D) embedded in concrete slab were removed and examined for micro-structure.

3.1 Comparison of tensile strength in bare steel bars with AZ91D and pure Mg anode

Steel rods were taken out on the 20th, 40th, 60th and 80th days and tested for tensile strength in a 100 ton Universal Testing Machine for yield stress, ultimate stress and % elongation. The results for tensile test of AZ91D and pure Mg are presented in Fig. 2(a and b) respectively.

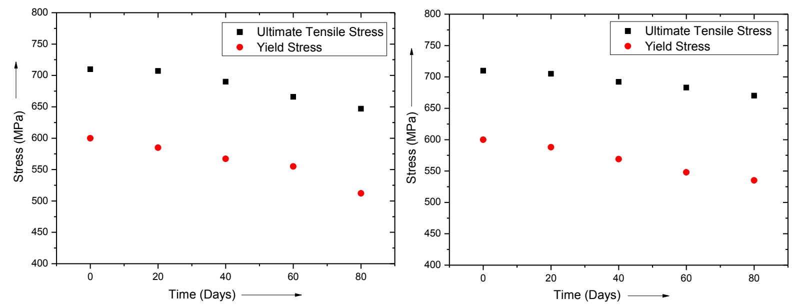

Fig. 2*. Yield stress and Ultimate tensile stress of steel reinforcement in MPa under high Chloride (7.5%) atmosphere with (a) AZ91D and (b) pure Mg.*

At the end of the test period, it is found that this reduction if percentage elongation is approximately 25% for reinforcements tied to AZ91D and pure Mg; although, reduction in case of AZ91D is observed to be slightly higher compared to pure Mg anodes.

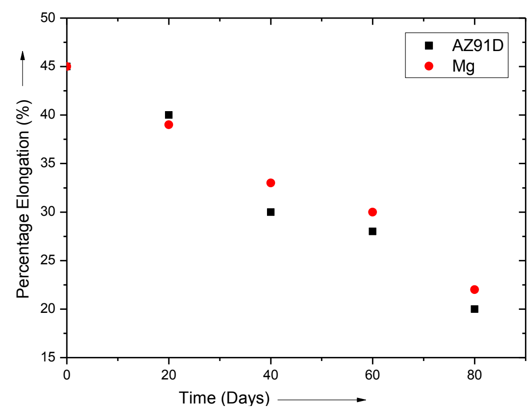

Fig. 3. *Percentage elongation of steel reinforcement under high Chloride (7.5%) atmosphere with AZ91D and pure Mg.*

3.2 Microstructure of corroded Anodes (Mg/ AZ91D) vs un-corroded

The anodes from the concrete was taken after 270 days of embedment and observed microscopically using Hitachi S-3400N SEM equipped with Energy Dispersive Spectroscopy (EDS). The analysis of samples was carried out with a 2 μm probe diameter, 10 kV accelerating voltage and 50 nA probe

Fig.3 (a-d). BSEI of corroded and un-corroded parts of pure Mg

current. The error of the SEM measurements is estimated to be about ± 2 at. %.

3.2.1 Micro-structure of pure Mg.

corroded and un-corroded parts of pure Mg after 270 days of embedment in concrete, with gradually increased magnification of the area of interest to systematically understand the features of the anode. Fig.3(a) shows the junction of corroded and un-corroded regions of the anode. Three distinct features could be observed in the micrograph,

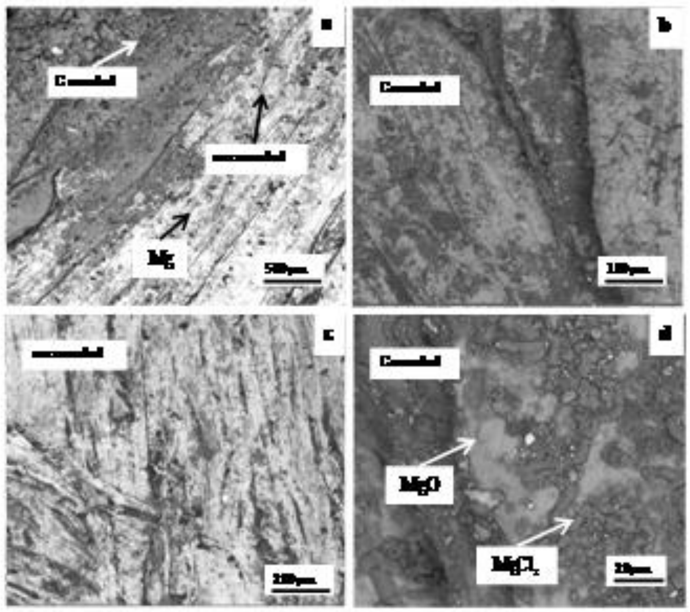

Fig.3 (a-d) *reveals the backscattered electron images (BSEI) of*

namely, white, grey and spots of darker shade of grey. EDS spot analysis was carried out to deduce the composition of these features. The spectral composition of white layer was found to be pure Mg, the grey layer consisted of MgO, while point analysis of the dark grey features confirmed the formation of MgCl2 in the corroded region. Fig. 3(b) and 3(d) show the magnified images of the corroded regions, while Fig.3(c) shows the un-corroded region. It could be seen that there are grey regions in the pure Mg due to formation of MgO.

3.2.2 Micro-structure of AZ91D.

BSEI of the unpolished as-cast alloy revealed that the macro-scopically smooth alloy anode actually consisted of ridges or protrusions (Fig.4(a)). The EDS spot analysis revealed that these ridges were composed of MgO roughly 20μm long. The micro-structure of polished un-corroded as-cast sample of AZ91D is shown in Fig.4(b). The objective to analyze the micro-structure of polished sample was to understand the internal structure of the alloy. It consists of Mg matrix and inter-metallics with well developed primary dendrites distributed along the α-Mg grain boundaries. The inter-metallics consist of Mg17Al12 (dark grey) and Al2Mg5Zn2 (light Grey). Thus, the three phases are in equilibrium in the ternary alloy and have a eutectic composition.Fig. 4(c) shows the BSEI of the corroded AZ91D alloy after 270 days of embedment. It consists of irregular oxide nodules (primarily MgO) of varying sizes ranging from 5-40 μm formed due to oxidation of α-Mg matrix and craters of MgCl2 along with the matrix phase. The oxide nodules were formed preferentially at grain boundaries, while craters of MgCl2 were randomly distributed. The craters have pores which might have formed due to the chemical reaction of Mg+ ions of the Mg matrix with H2O. The pertinent equations are as follows:

$$Mg \rightarrow Mg^+ + e^- \quad (1)$$

$$2Mg^+ + 2H_2O \rightarrow Mg^{2+} + Mg(OH)_2 + H_2 \quad (2)$$

It could be observed that Mg17Al12 phase acts as a barrier as well as a potential site for cathodic reaction. Similar observations were reported by Jonsson and Perrson. (Jönsson). Further, area analysis of 400 μm (Fig.4. (d)) of sample shows the findings discussed above pictographically.

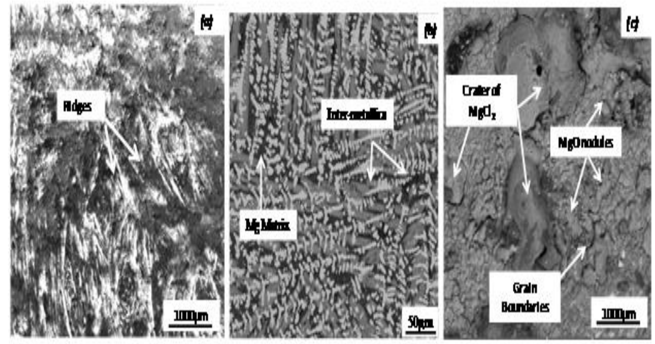

Fig.4. (a) *BSEI of unpolished as-cast AZ91D, (b) BSEI of the corroded AZ91D alloy after 270 days of embedment*

CONCLUSION

Investigation of the mechanical properties of steel in electro-chemical contact with pure Mg and AZ91D anodes using concrete with 3.5% NaCl by weight of cement and using bare steel in 7.5% NaCl dissolved in tap water and micro-characterization of corroded anodes was undertaken in the current work. The yield stress and ultimate tensile stress were found to decrease by approximately 50MPa while the reduction in percentage elongation is approximately 25% for reinforcements tied to AZ91D and pure Mg at the end of 80 days compared to fresh steel reinforcement. The mechanical properties of steel coupled with both the anodes showed similar results but the rate of corrosion of pure Mg was reportedly slightly higher compared to AZ91D due to the presence of inter-metallics as inferred through micro-graphs.

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