Electrochemical behavior of SmCo (2:17) based magnetic alloy in marine environment at room temperature

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Abstract. Corrosion resistance behaviour of Potentio-dynamic polarization and electrochemical impedance spectroscopy measurements are used to investigate the effects on the corrosion resistance behaviour of Sm2Co17 in Cl− containing environment. The experiments were conducted in 3.5wt% NaCl solution at 25 °C for one day. During the 24hours immersion, the corrosion current of Sm2Co17 magnet changed from 5.679x10^-6 to 1.03x10^-5 A/cm² and there was no apparent changed in magnetic properties measured at 25 °C after corrosion tests. Microstructure study results showed the material response to pitting corrosion which alternately emphasized the importance of surface engineering.

1. Introduction
SmCo (2:17) based rare earth permanent magnets possess marvelous magnetic properties and maximum Curie temperature. They have garnered an enormous research interest and their application spread into the industry of aero-engines and military [1, 2]. Despite of their advantages, they have a serious drawback of surface oxidation when temperatures goes beyond 500 °C [3-7]. In order to address this shortcoming, many strategies have been devised such as alloying additives and surface modification. The former method improves the oxidation resistance, however, due to additives reinforcement effect the intrinsic coercivity Hc, which lowers the magnetic properties. Thus later method, is a feasible approach due to its extrinsic effect only [8, 9].

Corrosion attack due to environment limits the applications of SmCo based alloys in generators of turbines but corrosion resistance behavior study of these alloys is scare. Previous studies have investigated corrosion behavior of NdFeB and SmCo5 permanent magnets and emphasize on surface engineering to improve corrosion resistance behavior [10-14].

The main aim of present study is to investigate the corrosion resistance behavior of SmCo (2:17) based alloy in neutral 3.5wt% NaCl solution.

2. Experimental work
Sm (Co0.16Fe0.16Cu0.06Zr0.03)7.6 magnetic alloy was prepared by conventional powder metallurgy process under 200MPa in 5T magnetic field orientation followed by heat treatment method in Ar atmosphere at 1213°C for 5h which lead to isothermal aging at 820 °C for 24h and finally slow cooling and quenching at room temperature. Specimens with dimension (10×10×5) mm were cut from the bulk material, polished with silicon carbide grit 100 and ultrasonically degreased in acetone and rinsed with deionized water for 3-5mints. Magnetic properties were measured with NIM-500. Corrosion test was carried out in 3.5wt% sodium chloride electrolyte with pH 7.0 at 25 °C. Potentio-dynamic polarization (PC) and electrochemical impedance spectroscopy (EIS) measurements (5mV SA, 10^-5-10^-2 Hz ) were executed
for corrosion evaluation of material where three electrodes system with platinum (Pt) as counter electrode, saturated calomel electrode (SCE) and sample (1cm² exposed area) as reference and working electrode were used respectively. Microstructure studies were carried out with the scanning electron microscopic (SEM) analysis.

3. Results
Prior to consider the application of magnetic materials in corrosive environment the effects on their magnetic properties and their physical appearance in harsh environmental conditions are worth examining.

3.1. Magnetic properties change
Magnetic properties of Sm₂Co₁₇ magnetic alloy were measured before and after 24h immersion in 3.5% NaCl solution at room temperature. As it can be seen in table.1 that there is a slight decrease which is negligible. We can say that after 24h immersion in corrosive atmosphere at room temperature there was no effect on magnetic properties.

| Specimen  | Time (h) | Magnetic properties | Variations (%) |
|-----------|----------|---------------------|----------------|
| Sm₂Co₁₇  | 0        | 0.81 148.31 0.72    | -              |
|           | 24       | 0.80 148.10 0.71    | 1.2,0.41,1.4   |

3.2. Open circuit potential
Open circuit potential values of Sm (Co₀.₁₆Fe₀.₇₄Cu₀.₀₈Zr₀.₀₃)₀.₇₆ substrate in 3.5% NaCl solution at room temperature with different time intervals during 24hours immersion were conducted. With increasing time immersion OCP values moved toward more –ive direction as given in Fig.1 which indicates that material has tendency of corrosion in NaCl environment.

Figure 1 Open circuit potential as a function of time of the Sm₂Co₁₇ in marine environment.

3.3. Potentiodynamic polarization curves
The cyclic polarization curves during 24 hour immersion in marine environment are shown in Fig.2. It can be seen that at 0 and for 24h immersion in 3.5wt% NaCl solution, the backward scans of the Sm₂Co₁₇ magnetic alloy are below the forward scans indicating the liability of material to pitting corrosion. Values of corrosion potential (E₉₉₉) and current density (i₉₉₉) are derived from Fig.2 and given in table.2. It can be noted that the E₉₉₉ dropped from -0.59 to -0.70V while i₉₉₉ becomes higher (1.03x10⁻⁵) which
may be allotted to the damage of the any protective oxide layer which material surface tried to form during the 24h immersion in salt atmosphere.

Table 2 Electrochemical parameters derived from fig.2

| Specimen | Immersion Time (h) | Corrosion potential $E_{corr}$ (V/SCE) | Corrosion current $i_{corr}$ (A/cm$^2$) |
|----------|-------------------|--------------------------------------|---------------------------------------|
| Sm$_2$Co$_{17}$ | 0 | -0.59 | 5.679x10$^{-6}$ |
|          | 24 | -0.70 | 1.03x10$^{-5}$ |

Figure 2 Polarization curves of the Sm$_2$Co$_{17}$ in marine environment.

3.4. Electrochemical impedance spectroscopy test

For corrosion evaluation electrochemical impedance measurements are very helping and forthcoming methods. A small amount of amplitude signal is applied and the material response is noted in the form of frequency with magnitude and phase shift change at different frequency. The corrosion behaviour of material is then represented in resistance, inductance and capacitance components of a corrosion cell. EIS measurement of Sm$_2$Co$_{17}$ permanent magnetic alloy in 3.5wt% NaCl solution at room temperature with different time immersion are expressed in Nyquist and Bode plots in Fig. 3. At it can be seen that at 0h without immersion Sm$_2$Co$_{17}$ alloy have one capacitive loop of high frequency and one inductive loop of low frequency and this inductive loop shows the material response to pitting corrosion. But after 24h immersion in marine environment the diameter of semicircle vividly decreases.

Figure 3 (a) Nyquist and (b) Bode plots of Sm$_2$Co$_{17}$ in marine environment.
In order to clearly understand the corrosion mechanism, equivalent electrical circuit is drawn in Fig.4 which are derived from fitting the Nyquist data by using the ZsimpWin software. During the 24h immersion, model R(C(R(CR))) is used. In Fig.4, Rs is solution resistance of the corrosive electrolyte (3.5wt% NaCl), CPE1 equals to oxide layer capacitance (if formed), Re represents the electrical resistance of the oxide layer to the ionic conduction of ions, CPE2 is double film capacitance and finally Rct is the charge transfer resistance of the magnetic alloy. The fitted values from circuits are given in table 3. It can be observed that the values of both Re and Rct decrease in the corrosive conditions showing the magnetic alloy has poor electrical resistance and charge transfer resistance which allowed the material to get corrode by pitting corrosion and microstructure analysis further verified the pitting corrosion.

![Figure 4 Equivalent electric circuit of Nyquist diagram.](image)

**Table.3 EIS parameters derived from fig.4 by simulation**

| Specimen   | Immersion Time (h) | Rs (Ω.cm²) | CPE1 (F/cm²) | n | Re (Ω.cm²) | CPE2 (F/cm²) | n | Rct (Ω.cm²) |
|------------|--------------------|------------|--------------|---|------------|--------------|---|-------------|
| Sm2Co17    | 0                  | 19.23      | 1.75 x10⁵    | 0.85 | 97.78     | 1.5 8x10⁻⁵   | 0.5 | 45.02       |
|            | 24                 | 10.21      | 3.57x10⁻⁵    | 0.75 | 23.01     | 4.7x10⁻⁶     | 0.3 | 24.21       |

3.5. Microstructure analysis

Microstructure study were carried out by SEM before and after 24h immersion of Sm2Co17 magnetic alloy in 3.5wt% NaCl solution at room temperature. Before immersion in marine environment in Fig.5(a) magnetic alloy surface have shown the presence of white spots with the compositions of Sm2O3 which is due to the high infinity of Sm towards oxygen that even during the polishing and cleaning of samples caused the oxidation of Sm element. After 24h immersion (Fig.5 (b)) big close and open pits appeared on the surface of magnetic alloy. Sm2Co17 alloy has structure with different phases and compositions which result in different potential corrosion cells with +ve (anode) and –ve potential (cathode) across the whole surface causing the anode area to corrode as a result pits appear on the surface effecting the material physical integrity and its usefulness in the respective application.

![Figure 5 SEM images of Sm2Co17 permanent magnetic alloy (a) before and (b) after immersion in marine environment](image)
4. **Importance of surface engineering**

Rare earth permanent magnet Sm$_2$Co$_{17}$ has unique magnetic properties which are ensured by the multiphase structure containing Sm$_2$Co$_{17}$, SmCo$_5$ and Sm-rich phases but at the same time this kind of structure makes magnetic material highly susceptible to oxidation and corrosion. Due to the high chemical activity of Sm-element around the matrix and different potential difference around the phases caused the pitting corrosion in Sm$_2$Co$_{17}$ magnet. This type of corrosion increase the material brittleness and thus material failure in respective application. A schematic representation of corrosion mechanism in Sm$_2$Co$_{17}$ magnetic alloy in marine (3.5wt% NaCl solution) environment is given in Fig.6. Addition of foreign elements to rare earth permanent magnets to overcome the oxidation and corrosion problem has not been very helpful. Surface engineering can solve the problem and improve the oxidation and corrosion resistance without affecting the magnetic properties and changing the alloy structure. The surface modification technique is effective and economical. Use of coating technique and suitable coatings depends upon the nature of material and its application field.

![Figure 6. Schematic representation of corrosion process in Sm$_2$Co$_{17}$ permanent magnetic alloy in marine environment.](image)

5. **Conclusion**

The study of corrosion characteristics of Sm$_2$Co$_{17}$ permanent magnetic alloy was conducted systematically in simulated marine environment at room temperature. The results demonstrated that the decrease in magnetic properties was not prominent for 24hours immersion in 3.5wt% NaCl solution. Nevertheless, the material under question could not develop protective oxide film and was highly susceptible to pitting corrosion. On the basis above results, the importance of surface modifications by suitable coatings is obvious.

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