NUST Journal of Engineering Sciences, Vol. 10, No. 1, 2017, pp. 14-18

Graphene oxide coating for improved corrosion resistance of NdFeB

Mohsin Ali Raza[1*], Akhlaq Ahmad[2], Faizan Ali Ghauri[1], Abdur Rehman[2], Rafiq Ahmad[1]
[1]Department of Metallurgy and Materials Engineering, CEET, University of the Punjab, Lahore, Pakistan
[2]University of the Engineering and Technology, Lahore, Pakistan
*mohsin.ceet@pu.edu.pk

Received: 5 May 2016 Accepted: 2 Feb 2017

Abstract

Electrophoretic deposition (EPD) of graphene oxide (GO) was carried out on Neodymium iron boron (NdFeB) magnets to study its potential as corrosion resistant coating. GO was produced from powder graphite by Hummers method. The GO was obtained by sonicating graphite oxide/water suspension and GO coatings were deposited on NdFeB magnets by making magnets anode in EPD process and by keeping voltage 10 V and time of deposition 1-2 min. GO and GO coating morphology and structure were studied by atomic force microscopy and x-ray diffraction, respectively. Electrophoretically deposited GO coatings on NdFeB were fairly uniform with some porosity. Potentiodynamic polarization and electrochemical impedance spectroscopy were used to study corrosion behavior of the GO coatings. GO coating reduced the corrosion rate of NdFeB by three times than the bare metal. The results show that GO coatings offer excellent corrosion resistant to NdFeB magnets in 3.5 % NaCl solution.

Keywords: NdFeB, Electrophoretic deposition, Coating, Corrosion, Graphene oxide

Introduction

Graphene is an atomic layer of sp2 bonded carbon atoms packed in a honeycomb-like lattice. It has gained a huge interest in a number of fields due to its fascinating properties such as high electronic conductivity, superior chemical stability, high thermal conductivity and excellent mechanical properties [1, 2]. Graphene and its derivatives, GO or functionalized graphene, based coatings can provide an excellent barrier to ionic transport without alteration of metal underneath due to their two-dimensional morphology, and this makes them interesting coating materials for enhancing corrosion resistant of electrochemically active metals. Several studies demonstrated improvement in the corrosion resistance of metals by graphene coatings [3-5].

Neodymium iron boron (NdFeB) magnets are widely used in several mechanical equipments due to their excellent magnetic properties [6]. Unfortunately, NdFeB magnet exhibits poor corrosion resistance in specific environments which limits its use. Mostly NdFeB magnets are manufactured through powder metallurgy route resulting in porous and multiphase microstructure [7, 8]. NdFeB microstructure consists of three basic phases: (i) matrix phase ($Nd_2Fe_{14}B$), (ii) Nd-rich phase (Nd_4Fe) and (iii) B-rich phase ($NdFe_4B_4$) [9]. The Nd-rich phase has the highest electrochemical activity due to high rare earth content. Anodic dissolution of the Nd-rich phase can occur at potentials more negative than the corrosion potential of the NdFeB magnet [10] resulting in the shorter service life of NdFeB magnets [11, 12]. Improving corrosion resistance of the NdFeB magnets is of great interest for researchers and manufacturers. Currently, NdFeB magnets corrosion resistance is enhanced by multilayered electrodeposited coatings such as Ni-Cu-Ni coatings, which offer sufficient corrosion protection. However, chemicals employed for electrodeposited coatings are not environmentally friendly and there is always a room for producing better coatings.

This work aims to deposit GO coatings on the surface of the NdFeB magnets. GO coatings are light weight compared to electrodeposited coatings and can have minimum effect on the magnetic properties of NdFeB magnets, unlike Ni-based coatings which are magnetic in nature. Most of the literature has focused on depositing graphene on metals via chemical vapor deposition (CVD) method. In present work Electrophoretic deposition (EPD) is utilized to deposit GO coating on NdFeB magnets. EPD is an alternative and environmentally friendly method for the deposition of GO on metallic substrates. It produces coatings at room temperature with uniform thickness, high deposition rate, and does not deteriorate metallurgical features of metals [13].

The main aim of this work was to deposit GO coatings on NdFeB magnets by EPD technique. The resulting coatings were characterized and their corrosion resistance performance was studied by potentiodynamic polarization and electrochemical impedance spectroscopy in 3.5 % NaCl solution.

Experimental

Materials and Chemicals

Sri Lankan grade powder (SG-graphite) was used in this study which had an average particle size between 100–200 µm. Sodium nitrate ($NaNO_3$), sulphuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), and ethanol all analytical grade chemicals were used. NdFeB magnets in the form of pellets (diameter 10 mm and thickness 5 mm) were purchased from local market. The as-purchased magnets were nickel-copper plated. The electrodeposited metal was removed by rough grinding to expose a fresh surface of NdFeB for coating.

Synthesis of Graphite Oxide

Graphite oxide (GO) was synthesized from graphite powder (SG-graphite) by using Hummers method [13]. Briefly, concentrated H_2SO_4 was added to a mixture of graphite powder (2 g) and $NaNO_3$ (1 g) with continuous magnetic stirring in three neck flask kept at a temperature less than 5 °C. After 2 hours, $KMnO_4$ (6 g) was slowly added to the above solution to prevent the sudden rise of temperature. After 30 min of stirring 92 ml of warm water was added gradually to the mixture, then further 280 ml water was added. At the end of the reaction, 3 ml of (30 %) H_2O_2 solution was added drop-wise to remove excess $KMnO_4$. Finally, the solution was filtered and washed with deionized water to obtain neutral pH. The retrieved graphite oxide powder was dried at 50 ºC in a vacuum oven.

Deposition of Coating

NdFeB pallets were ground on silicon carbide papers (180 to 1200 grit sizes). After surface preparation, samples were sonicated in ethanol for 15 min to remove any surface contaminants. Graphite oxide powder 3 mg ml-1 was dispersed in deionized water by sonication for 3 hours at 40 ºC to obtain a stable suspension of GO. The ultrasonication exfoliates graphite oxide to GO. For EPD, NdFeB samples were made as anode and platinum was used as a cathode in the EPD cell. Optimization of EPD process was achieved and it was found that a uniform coating of GO can be obtained at 10 V for 2 min using DC voltage source. All coatings studied in this work were produced under similar conditions.

Characterization

X-ray diffraction (XRD) analysis of the graphite oxide powder (produced via Hummers method) was conducted by diffractometer (Bruker). Atomic force microscopy (AFM) images of GO were obtained after depositing a GO-water suspension on a mica substrate using tapping mode AFM (Solver Nano, NT-MDT, Russia). GO coatings on NdFeB were also investigated using contact mode AFM to determine uniformity and thickness of the coating. Coating thickness was measured by scanning that area of the coating where some pores were seen.

Electrochemical studies were conducted in the three-electrode cell using potentiostat/galvanostat/ZRA (Reference 3000, Gamry Instruments, Inc., USA). NdFeB pellets and GO-coated pellets were made as working electrode, a platinum wire as a counter and a saturated calomel electrode as a reference electrode which was immersed in 3.5 % NaCl electrolyte solution. Potentiodynamic polarization scan was performed to determine coating response to DC voltage. Potentiodynamic polarization overvoltage in the range of -0.5 V to 1.5 V (vs open circuit potential (OCP)) at a scan rate of 5 mV/sec was used. Electrochemical impedance spectroscopy (EIS) was conducted at an amplitude of ±10 mV (rms) within a frequency range of 10 mHz to 100 kHz. All tests were performed after stabilizing OCP.

Results and Discussion

Characterization

XRD pattern of graphite oxide and GO coated NdFeB magnet is shown in Fig.1. Graphite shows a sharp peak at 26.84^0 corresponding to the (002) crystal plane. After oxidation of graphite by Hummers method, the intensity of (002) diffraction peaks is weakened and a broad peak at 8.5° was observed which correspond to the (001) crystal plane of graphite oxide. The interplanar spacing of (001) was increased to ~1.039 nm which is considerably larger than (002) crystal plane spacing. The significant increase in the layer spacing confirms successful oxidation of graphite, which is the source for the production of GO by ultrasonication in solvents. The graphite oxidation is due to intercalation of sulfate ions and hydroxyl ions in the galleries of graphite. Hummer's process also excessively produce epoxide groups on the basal planes of graphite and carboxylate and hydroxyl groups on the peripheries of basal planes [14].

XRD pattern of GO-coated NdFeB magnet (Fig. 1) shows only the peaks due to NdFeB magnet, indexed in Fig. 1 according to [15], and no (002) or (001) peaks of graphite or graphite oxide. It can be vaguely said that that graphene coating has been deposited on the NdFeB magnet. However, to confirm this XRD thin film analysis of coating should have been done, because conventional XRD has a limitation in getting diffraction from very thin films.

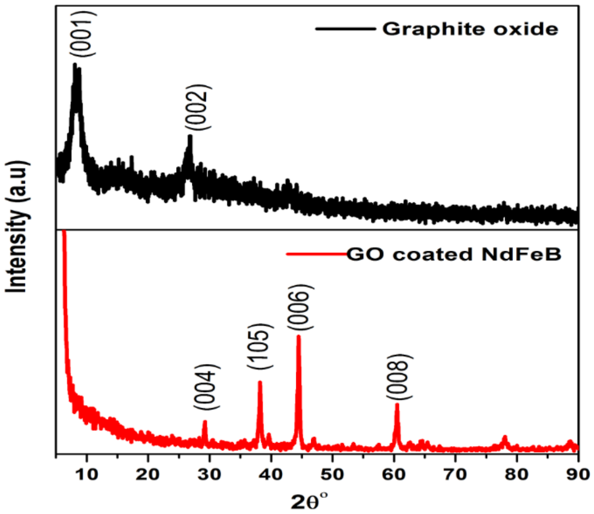


Fig. 1: XRD of graphite oxide and GO coated NdFeB magnet. Indexing of GO and GO coated NdFeB magnets is also labeled

Coating Morphology

The AFM image obtained in tapping mode (Fig.2 (a)) and lateral force microscopy (Fig.2 (b)) shows that GO has a thickness in the range of 1-2 nm and average lateral size of 70-400 nm.

The contact mode AFM images of NdFeB magnet is presented in Fig. 3. The surface of the NdFeB sample was very smooth as can be seen with Ra value of 4.3 nm. All samples of magnets on which GO was deposited had a similar level of roughness. On the other hand, the surface of GO-coated NdFeB sample was found much rougher (Ra = 162 nm) than the bare NdFeB magnet as can be seen from the contact mode AFM image of GO coated NdFeB samples (Fig. 4). The increased roughness of coated magnet suggests random deposition of GO coatings. The wrinkled morphology of GO might also be responsible for increased roughness of coating. Fig. 4(a) of GO-coated NdFeB magnet shows coating thickness around 1-1.5 µm with particulate morphology. This suggests that the particles deposited on one another to build a thick film of ~1 µm and this has happened in just less than 2 min of deposition. Some pores in the coatings can also be seen. The SEM image of the GO coated NdFeB magnet is shown in Fig 4(b). The GO coatings are uniformly deposited on the metal surface, however, some defects (pore) in the coating can also be seen. It is not clear whether there is a film of GO at the base of the pore or not.

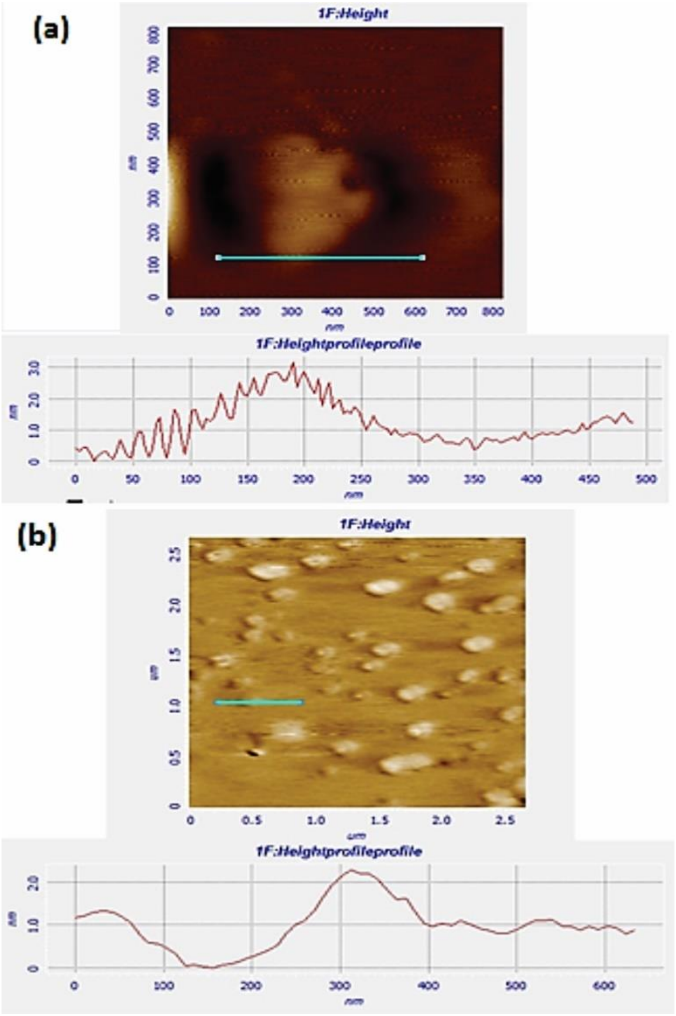
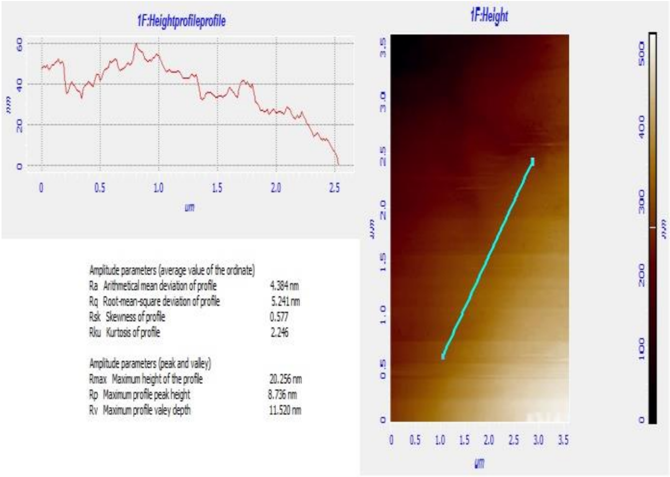


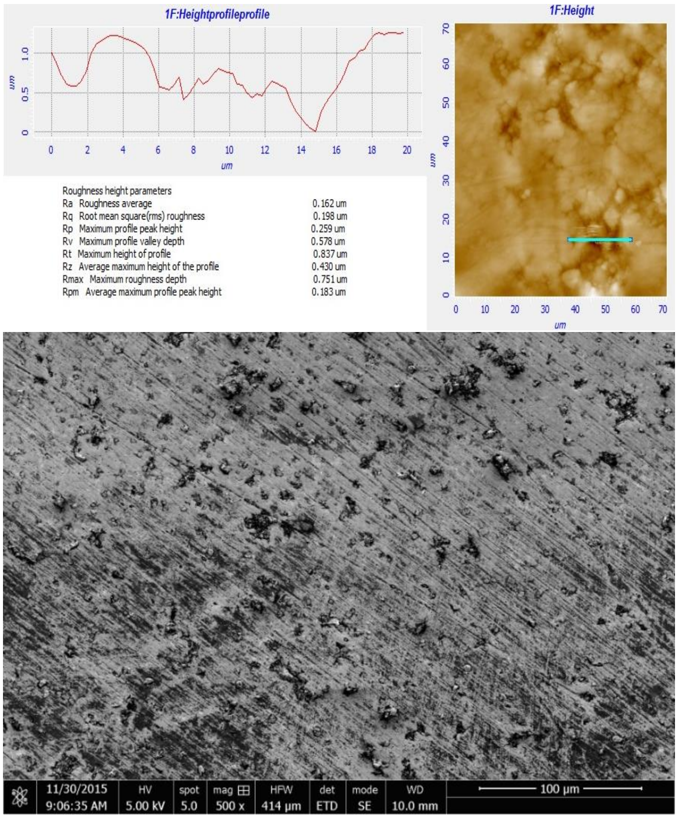
Fig. 2: (a) Tapping mode AFM image of GO (b) Lateral force AFM image of GO



Amplitude parameters (average value of the ordinate)	
Ra Arithmetical mean deviation of profile	4.384 nm
Rq Root-mean-square deviation of profile	5.241 nm
Rsk Skewness of profile	0.577
Rku Kurtosis of profile	2.246

Amplitude parameters (peak and valley)	
Rmax Maximum height of the profile	20.256 nm
Rp Maximum profile peak height	8.736 nm
Rv Maximum profile valley depth	11.520 nm

Fig. 3: Contact mode AFM image of bare NdFeB magnet on which GO was deposited by EPD process. Surface roughness parameters and height profile are also shown.



Roughness height parameters	
Ra Roughness average	0.162 um
Rq Root mean square(rms) roughness	0.198 um
Rp Maximum profile peak height	0.259 um
Rv Maximum profile valley depth	0.578 um
Rt Maximum height of profile	0.837 um
Rz Average maximum height of the profile	0.430 um
Rmax Maximum roughness depth	0.751 um
Rpm Average maximum profile peak height	0.183 um

Fig. 4: (a) Contact mode AFM image of bare NdFeB magnet on which GO was deposited by EPD process and (b) SEM image of the GO coating.

Corrosion Study

Potentiodynamic polarization curves are shown in Fig. 5. Anodic and cathodic current densities are reduced showing a decrease in corrosion current. Icorr is decreased from 1240 μAcm−2 for bare NdFeB to 326 μAcm−2 for GO-coated NdFeB magnet with a positive shift in Ecorr (58 mV) which clearly demonstrates increased corrosion resistance of NdFeB. The results obtained using Echem analyst software (Gamry Instruments) are shown in Table 1. These results are in agreement with the findings of Liu et al. [16].

In an aggressive environment like NaCl, dissolution of NdFeB magnets occurs by the anodic reactions (I) and (II). The Nd-rich phase is anodic then other phases, so certainly dissolution of magnet initiates from this. This reaction forms passive hydroxide film on the magnet to protect it from environment further. However, aggressive Cl- can penetrate through the interface which damage passive film and expedite dissolution of NdFeB magnet. GO-coated NdFeB magnet showed less anodic current density as compared to the bare magnet which proves that GO coating improved the corrosion resistance of NdFeB.

$$\mathrm{Nd} \rightarrow \mathrm{Nd}^{3+} + 3\mathrm{e}^{-} \quad \text{(I)}$$

$$\mathrm{Nd}^{3+} + 3\mathrm{OH}^{-} \rightarrow \mathrm{Nd}\,(\mathrm{OH})_3 \quad \text{(II)}$$

EIS was performed to further evaluate the electrochemical response of GO coating. Fig. 6 shows Nyquist and Bode curves for coated and bare NdFeB pellets. In Nyquist plot (Fig. 6(a)) area of curve reflects the resistance to electron transfer i.e, corrosion resistance. Higher the electron charge transfer, higher

Table 1: Kinetic parameters obtained from potentiodynamic polarization curves.

Samples	Beta A (V/decade)	Beta C (V/decade)	E_{corr} (mV)	I_{corr} (µA/cm²)	Corrosion Rate (mpy)
Bare	0.368	0.166	-1050	1240.0	4478
EPD-GO	1.262	2.293	-992.0	326.0	1177

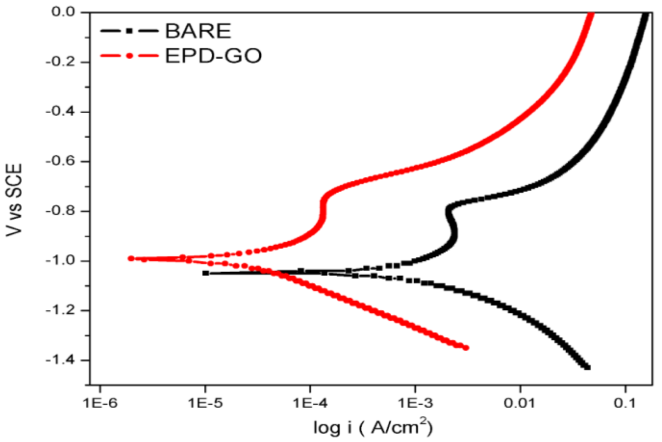


Fig. 5: Potentiodynamic polarization curves of bare NdFeB and GO-coated NdFeB magnets

will be the corrosion resistance of the metal. Bare NdFeB had a charge transfer resistance of 42 ohmcm2, whereas the GO-coated NdFeB had higher than 100 ohmcm2, suggesting a very high corrosion resistance of the latter. In Bode plot (Fig.6 (b)), the impedance in the low-frequency region indicates the corrosion resistance of a metal. Fig.6 (b) shows higher impedance value for GO-coated NdFeB (110 ohm.cm2) than bare NdFeB (50 ohm.cm2) confirming potentiodynamic data that GO-coated NdFeB offers higher corrosion resistance. The EIS results are consistent with polarization results of the same samples. It can be seen from Fig.6 (b) that middle-frequency impedance of both bare NdFeB and GO-coated NdFeB resembles, which suggests double layer capacitance phenomena of both bare NdFeB and GO-coated NdFeB magnets, and hence both favored charge collection in a similar way. However, at higher frequency impedance of GO-coated NdFeB is higher than bare NdFeB (Fig.6 (b)), suggesting that GO-coating had completely covered NdFeB

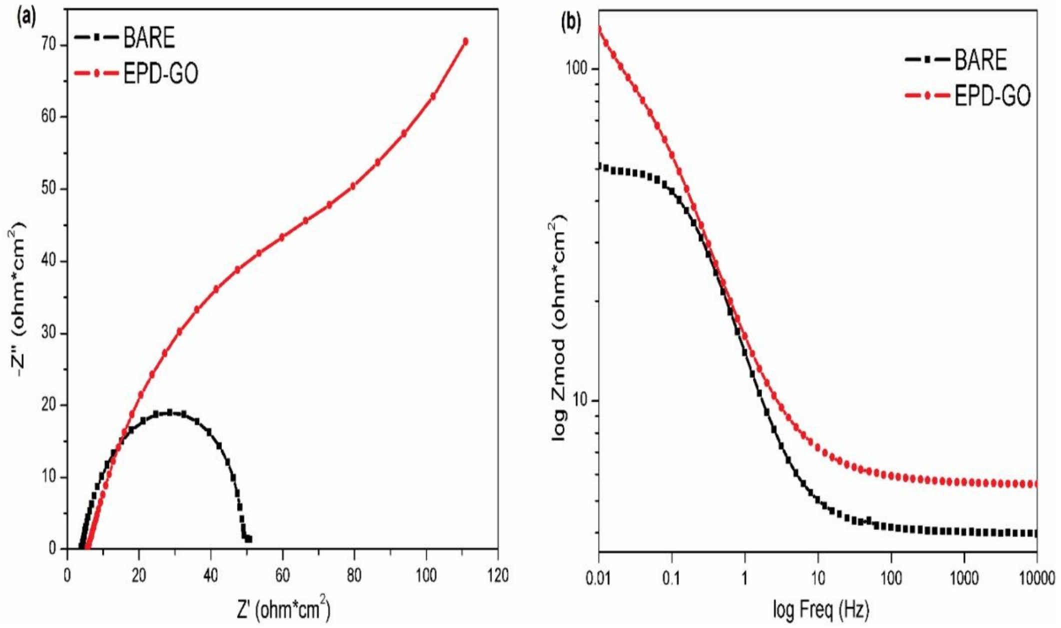


Fig. 6: EIS results (a) Nyquist curve (b) Bode plot of bare NdFeB and GO-coated NdFeB magnets performed in 3.5 % NaCl solution.

Conclusions

GO coating of almost 1 µm on NdFeB magnet was successfully deposited from ultrasonicated graphite oxide/water suspension using EPD process. GO thickness was found in the range of 1-2 nm. The thicknesses of graphene coatings were found ~1-2 µm by AFM microscopy. The coatings' morphology was found to be particulate-like and coated films were found much rougher than bare NdFeB magnet due to the crumbly nature of GO as observed by AFM. The corrosion testing in 3.5 % NaCl solution revealed ~3× lower corrosion rates of GO-coated NdFeB magnets than bare metal. The GO coatings developed in this work are therefore promising in enhancing corrosion resistance of NdFeB magnets.

Acknowledgement

The authors would like to thank Higher Education Commission of Pakistan for providing financial support in conducting this research.

REFERENCES

1. Geim, A.K. and K.S. Novoselov, The rise of graphene. Nature materials, 2007. 6(3): p. 183-191.
2. Nair, R., et al., Fine structure constant defines visual transparency of graphene. Science, 2008. 320(5881): p. 1308-1308.
3. Bunch, J.S., et al., Impermeable atomic membranes from graphene sheets. Nano letters, 2008. 8(8): p. 2458-2462.
4. Sutter, E., et al., Monolayer graphene as ultimate chemical passivation layer for arbitrarily shaped metal surfaces. Carbon, 2010. 48(15): p. 4414-4420.
5. Chen, S., et al., Oxidation resistance of graphene-coated Cu and Cu/Ni alloy. ACS nano, 2011. 5(2): p. 1321-1327.
6. Ghandehari, M.H., Rare earth-iron-boron permanent magnets with enhanced coercivity. 1988, Google Patents.
7. Tokuhara, K. and S. Hirosawa, Corrosion resistance of Nd ‐ Fe ‐ B sintered magnets. Journal of Applied Physics, 1991. 69(8): p. 5521-5523.
8. Chang, K.E. and G.W. Warren, The effect of absorbed hydrogen on the corrosion behavior of NdFeB alloys. Magnetics, IEEE Transactions on, 1995. 31(6): p. 3671-3673.
9. Schultz, L., et al., Corrosion behaviour of Nd–Fe–B permanent magnetic alloys. Materials Science and Engineering: A, 1999. 267(2): p. 307-313.
10. Attanasio, S. and R. Latanision, Corrosion of rapidly solidified neodymium-iron-boron (Nd · Fe · B) permanent magnets and protection via sacrificial zinc coatings. Materials Science and Engineering: A, 1995. 198(1): p. 25-34.
11. Rada, M., et al., Corrosion studies on highly textured Nd–Fe–B sintered magnets. Journal of alloys and compounds, 2006. 415(1): p. 111-120.
12. El-Moneim, A. and A. Gebert, Electrochemical characterization of galvanically coupled single phases and nanocrystalline NdFeB-based magnets in NaCl solutions. Journal of applied electrochemistry, 2003. 33(9): p. 795-805.
13. Hummers Jr, W.S. and R.E. Offeman, Preparation of graphitic oxide. Journal of the American Chemical Society, 1958. 80(6): p. 1339-1339.
14. Daniel R. Dreyer, S.P., Christopher W. Bielawski, Rodney S. Ruoff, The chemistry of graphene oxide. The Royal Society of Chemistry, 2010. 39: p. 228–240.
15. Jin-Yuna, J., et al., Fine-grained NdFeB magnets prepared by low temperature pre-sintering and subsequent hot pressing. Chinese Physics B, 2014. 24(1): p. 493-497.
16. He, W., et al., Electrophoretic deposition of graphene oxide as a corrosion inhibitor for sintered NdFeB. Applied Surface Science, 2013. 279: p. 416-423.