Nano zinc oxide for efficient activation of aluminium zinc alloy sacrificial anode

B. Jabeera, T. S. Anirudhan and S. M. A. Shibli*

Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum-695581 INDIA

Abstract: *Zinc oxide nanoparticles were prepared by anodic dissolution of zinc metal strip under standardized experimental conditions. Aluminium zinc alloy sacrificial anodes reinforced with the zinc oxide nanoparticles were fabricated for application in cathodic protection of steel articles. The process of reinforcement with the particles not only improved the metallurgical properties of the anode but also the galvanic performance of the anodes significantly. The anode reinforced with the optimum quantity of the composite (1%) exhibited a galvanic efficiency as high as 94%. The anode exhibited high and steady anode potential, very low polarisation and very low self-corrosion during a prolonged galvanic exposure studies conducted with sodium chloride solution. The present results have further merits in terms of low cost, non-toxicity and easy disposal.*

Key words : zinc oxide, nanoparticle, cathodic protection, aluminium alloy, sacrificial anode.

1. INTRODUCTION

The current generated in the sacrificial anode in a cathodic protection system depends on the physicochemical and electrochemical properties of the anode, its efficiency and geometry. Aluminium is a good choice as sacrificial anode for cathodic protection due to its high current capacity, low specific weight, high electrical conductivity, nominal cost and easy availability. However pure aluminium cannot be used as sacrificial anode because its surface has passive alumina layer. To disrupt the physical integrity of the passive film, several alloys have been developed with different activators. Many investigators have reported that just 5% zinc addition into aluminium is optimum that yields good metallurgical and electrochemical characteristics of the aluminium alloy anode through formation of a β phase [1].

Conventionally, metals like tin, mercury, indium and bismuth are added as micro-dopends during casting of aluminium alloy sacrificial anodes [2-8]. Micro alloying with these elements results in subsequent activation of the underlying substrate metal. The metal oxides incorporation in such anodes can refine the

grains and their boundaries and suppress the grain boundary corrosion of the anodes, enhancing their galvanic performance [9-11]. Oxides of aluminium and manganese are also used for production of high wear resistance sacrificial anodes [9,11]. The incorporation of 5% Al_2O_3 in Al alloy anode can result in substantial metallurgical improvement of the alloy [9]. In the case of aluminium alloy composite anodes, the infiltration of the reinforcement network by molten Al and the homogeneity of the matrix are partially governed by wetting nature of the reinforcement and the chemical interaction between the reinforcement and the aluminium matrix [12-16]. Many reports available in the literature indicate that Al_2O_3 is not wetted by molten aluminium below 1000 ^{o}C and it is considered to be inert in molten aluminium [12,17]. In contrast, the wettability of Al_2O_3 in molten Al and the physical interaction between Al_2O_3 and the molten Al have also been reported [18]. The effect of addition of TiO_2 has been rarely investigated since 1970's when its role in fabricating dimensionally stable electrodes was well established [19-22].

The characteristics of metal oxides especially their metallurgical influence depends on the size, extent of chemical inertness, melting point, wettability towards the base metal and segregation properties. In this context, a study on incorporation of nano

*To whom correspondence should be addressed: Tel: +91 471 2412 903
E-mail address: smashibli@yahoo.com(S. M. A. Shibli)

metal oxide, well known for having the former three properties, in sacrificial anodes gains significance. No such attempt has been made in this direction so far [23]. The present work had the objective of investigating the effect of incorporation of nano zinc oxide for improvement of aluminium alloy sacrificial anodes.

2. EXPERIMENTAL METHODS

2.1 Synthesis of zinc oxide nanoparticles

The zinc oxide nanoparticles were prepared by anodic dissolution of pure zinc metal strip anode (2 x 6 x 1 cm). The dissolution was done against a larger area platinum mesh as the cathode in an electrolyte containing a suitable surfactant. The electrolyte was prepared by mixing a 4:1 ratio of aqueous tetra butyl ammonium bromide solution (0.1M) and acetonitrile. No precipitation or clogging etc was observed during the process. Nitrogen gas was sufficiently purged prior to the dissolution process to ensure complete elimination of dissolved oxygen. The solution was kept stagnant and the process was carried out at 30 ^{o}C.

In the present process, an anodic current density of 5-mA/cm^2 was impressed on the zinc anode from a standard d c power source and the cell voltage was maintained at – 0.370 volt between the electrodes that were kept 5 mm apart from each other. The duration of the process was fixed depending on the quantity of the zinc oxide to be produced. The particles started settling down during the course of the process and the precipitate was filtered through ordinary filter paper. The washed and dried mass of the zinc oxide was added to the homogeneous melt of aluminum zinc alloy during casting of the anodes at 700 ^{o}C. A silicon carbide rod was used to stir the melt.

2.2 Fabrication of the anodes

Many of the currently available reports deals with aluminium rich zinc alloy sacrificial anodes, where zinc destabilizes the formation of alumina on the anode surface. The concentration of zinc varies in the range between 3 to 5%. Addition of 5% zinc, as many investigators report, is the optimum that improves the metallurgical and electrochemical characteristics of the anode through formation of a β phase [1]. This combination of Al and Zn forms a homogeneous solid solution with uniform grain size and grain boundaries throughout the entire crystal lattice. In the present work, 95% aluminium + 5% zinc alloy anodes were cast after melting the cut aluminium and zinc ingots in a graphite crucible, kept in a muffle furnace, at 700 +/- 10 ^{o}C. The melt was stirred using a silicon carbide rod. The homogeneous melt was poured into a preheated graphite die of dimension of 5 x 3 x 1 cm^3. The required amount of the zinc oxide nanoparticles were added into the melt with sufficient stirring and poured into the die. The cast anodes were polished to '300', degreased, rinsed with distilled water and analysed /

tested. Different batches of the anodes having reinforced with varying concentration of nano zinc oxide were fabricated.

2.3 Electrochemical evaluation of the anodes

2.3.1 Self-corrosion

The anode coupons were immersed in 3% NaCl solution for about 90 days. The difference in the weight of the coupons before and after immersion was measured after pickling the anode coupons. The coupons were kept undisturbed mechanically and electrochemically using suitable support and complete insulation. The corrosion rate was calculated using the formula

Corrosion rate = Weight loss / surface area x time of immersion (g/cm^2/h).

The values were found reproducible.

2.3.2 Polarisation

The anodes were anodically polarized potentiostatically, against a larger surface area platinum counter electrode. A saturated calomel electrode was the reference electrode. The polarization experiments were repeated for testing the reproducibility. The anodes were equilibrated in the 3% NaCl solution for sufficient time prior to each polarization. A standard potentiostat (BAS, USA) was used.

2.3.3 Galvanic efficiency

The test anode and a suitable cathode of mild steel of larger surface area was coupled together and immersed in 3% NaCl solution for a period of 90 days. An ammeter was introduced in between the electrical connections of the anode and the cathode. The varying current passing in the circuit was continuously monitored and plotted in a graph to integrate the total current passed in the circuit as a result of dissolution of the anode. The weight of the anode before and after the immersion of the galvanic couple for a period of 90 days was measured after cleaning the anode by a standard procedure (ASTM G 31). From the actual weight loss measured, the theoretical current produced by the anode was calculated.

Galvanic efficiency = A x 100 / B, where

A: the actual current produced from the anode (measured)

B: the theoretical current supposed to be produced as per Faraday's Law.

These experiments were carried out with parallel couples to ensure reproducibility.

2.3.4   OCP and CCP

The open circuit potential of the anodes in 3% NaCl solution was continuously monitored since the introduction of the anode, with respect to saturated calomel electrode. The plot of OCP vs. time was interpreted in terms of the long-term reliability of the anode. The varying closed circuit potential of the test anode with respect to a saturated calomel electrode was continuously monitored when the anode was coupled with a mild steel cathode and the couple was kept immersed in 3% NaCl solution. The CCP variation was monitored for a period of 90 days. These CCP data were considered more reliable in terms of simulating the actual system, than the polarization data. While the former is due to galvanic polarization the latter is due to galvanostatic polarization.

3.   RESULTS AND DISCUSSION

3.1   Characterisation of the zinc oxide particle

The zinc oxide nanoparticles were analyzed using a Hitachi H-600 TEM instrument. It was dip-coated on an amorphous carbon coated TEM grid and the samples were viewed at different magnifications (Fig. 1. A). The average size of the particles was found to be less than 25 nm as determined manually from the original images. A homogeneity in the mass of the sample was confirmed when it was viewed at different sites of the grid. The sample coated on the TEM grid after different periods of initiation of the dissolution process also revealed the same. The sample was colloidal and amorphous in nature; its diffraction pattern also clearly confirmed the amorphous character (Fig. 1.B). The diffraction pattern had a halo ring indicating the amorphous nature of the particles [24].
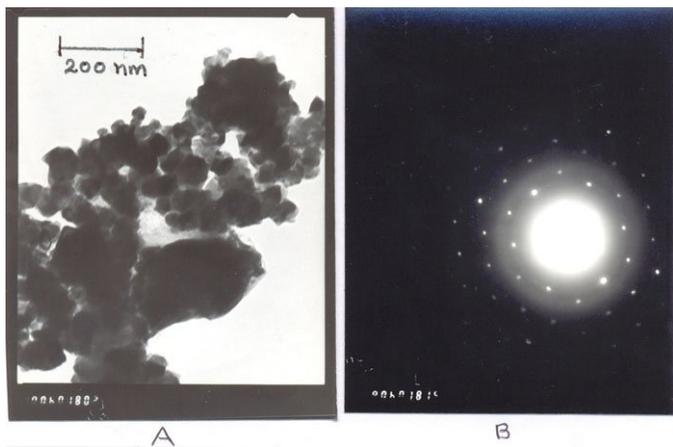
Figure 1: A. The TEM micrograph of zinc oxide at one lakh magnification B. The diffraction pattern of the zinc oxide nanoparticles.

The zinc oxide nanoparticles produced by the anodic dissolution process was filtered using ordinary filter paper and washed. The dried sample was analyzed by using an X-ray diffractometer (D-5005 Siemens using Cu Kα 1 radiation). The XRD pattern revealed the characteristic peaks of zinc oxide. The characteristic peaks also revealed 100, 002 and 101 planes of the sample. The confirmation that the particles were only metal oxides and not pure zinc indicated that the metal oxidation process occurred simultaneously along with metal dissolution.

3.2   Metallurgical improvement of the anode

The morphology of the anodes was characterized first, as metallurgical improvement is the main parameter that can be significantly improved by means of incorporation of nano metal oxides. The anode was cross-sectional wise cut. The cut surfaces were polished to the extent of metallurgical grade using different grades of emery paper, etched using sodium hydroxide solution and viewed using a Hitachi S-2400 Scanning Electron Microscope. Figure 2 shows the micrographs of the anodes that were incorporated with 1% of nano zinc oxide. The grains in the anodes were found to be almost uniform in terms of its size and distribution. No other specific defects like void, channel and segregate were found. Existence of the nanoparticles at the grain boundaries may be the root cause for the metallurgical improvement of the anode as clearly evidenced in the figures. The role of nanoparticle reinforcement did not confine with the activation process (electrochemical) alone, it also caused substantial reduction in self-corrosion. The presence of nanoparticles in the grain boundaries was the cause for suppression of non-columbic loss of the grains and hence self-corrosion. Almost similar observations were made on the SEM micrographs of the other anodes containing different concentration of zinc oxide. However, they were found to be inferior in terms of their electrochemical performance.

The Vicker's hardness number of the 1% nano oxide incorporated aluminium alloy anode was found to be 41.28, which is slightly higher than that of the bare anode (39.92). The variation in the hardness numbers as the results of varying concentration of the nano zinc oxide was found to be low in magnitude. Since achievement of high galvanic performance was the objective of the present work, no in-depth study on metallurgical improvement of the anodes as a result of fabrication parameters, was attempted.

3.3   Electrochemical evaluation of the anode

3.3.1   OCP decay

Four different batches of the anodes containing different concentrations of zinc oxide nanoparticles, viz., 0, 0.1, 0.5, 1, 2% were selected and their galvanic performance were evaluated by using different techniques like anodic polarisation, O.C.P decay measurement, C.C.P variation measurement and determination

Table 1: Galvanic performance of Zinc oxide nanoparticles reinforced 95/5 Al-Zn alloy sacrificial anode (Electrolyte: 3% NaCl, Cathode : Mild steel, Temp = 30^0, Stagnant condition

S.No	Conc. of ZnO Nanoparticles %	O.C.P. V/SCE i=0.1mA/cm^2	CCP V/SCE at x10^{-6} g/cm^2/h	Self corrosion	Efficiency %	Energy Density Ah/kg
1	-	-0.930	-0.915	10.860	58	1520
2	0.1	-0.940	-0.940	1.501	41	1004
3	0.5	-0.950	-0.950	0.913	45	1170
4	1	-0.930	-0.930	0.117	94	2665
5	2	-0.975	-0.960	0.123	54	1527

of self corrosion and galvanic efficiency. Fig. 3 shows the O.C.P decay curves of 95/5 Al-Zn alloy SA reinforced with different concentrations of zinc oxide nanoparticles. All the zinc oxide incorporated anodes showed higher initial O.C.P than the bare anode that contained no zinc oxide nanoparticles. In all the zinc oxide incorporated anodes there was a slight fluctuation in the O.C.P values, up to 10 days of immersion, after which the O.C.P became stable. Even though all the zinc oxide incorporated anodes show higher O.C.P than the bare anode, the best one could not be ascertained based on these results alone. In this context monitoring of C.C.P variations, when the anodes are galvanically coupled with steel cathodes, drew much attention in terms of simulating the actual galvanic performance of the anodes.

3.3.2 CCP variation

Fig. 4 shows the C.C.P variation curves of the 95/5 Al-Zn sacrificial anodes reinforced with different concentrations of zinc oxide nanoparticles. All the zinc oxide incorporated anodes showed high cathodic initial C.C.P values around – 0.940 V Vs SCE, which was substantially higher than that of the bare anode. The current that was flowing in the circuit was around 1 mA/cm^2. The C.C.P values of the nano particles incorporated anodes remained almost constant with least polarization. Since the C.C.P values of all the anodes were found in a narrow range, much inference could not be obtained at this stage.

3.3.3 Anodic polarization

The anodic polarization curves of the anodes are shown in Figure 5. The bare anode showed an average performance of polarization. Incorporation of the anodes with lesser amount of nano oxides caused even adverse effect, when compared with the performance of the bare anode. Though higher concentration of the nanoparticles yielded lesser polarization than that of the bare anode, the optimum and critical concentration of the nanoparticle was found to be 1 %. The corresponding anode showed very low polarization.

3.3.4 Self corrosion

All the nano particles incorporated anodes exhibited a narrow variation in the values of O.C.P decay, C.C.P variation, and polarization. The self-corrosion of the anodes was determined to assess the non-coulombic loss. All the four anodes showed very negligible self-corrosion for a 3 months period, in 3% NaCl, i.e. in the range of 1.5 – 0.1173 x 10^{-6} gm/cm^2/h. The self-corrosion values are shown in Table 1.

3.3.5 Galvanic efficiency

The galvanic efficiency values of the four combinations are given in Table 1. The reinforcement by incorporation of lower concentration of ZnO nanoparticles of 0.1 and 0.5% had adverse effects, i.e. they showed anodic efficiency in the range of 41 to 45%, while showing good O.C.P, C.C.P and also self corrosion values. The bare anode showed an efficiency of 58.5%. The efficiency of 1% nano zinc oxide incorporated sacrificial anodes was remarkably as high as 94.2%. It should be pointed out that commercially available anodes have 80 – 90% efficiency.

Keeping 1% ZnO incorporation was found to be the best and optimum. Table 2 compares the galvanic efficiency of the anodes incorporated with different concentration of nanoparticles of ZnO. The efficiency was determined by accelerated tests of impressing an anodic current density of 1 mA/cm^2 on the anode coupled with mild steel cathodes, for a period of 5 hours. The anode incorporated with 1% ZnO nanoparticles, showed efficiency higher than that of the bare anode. The addition of higher concentration of nanoparticles of ZnO than 2% was tried, but heterogeneity in the Al-Zn alloy melt was noticed. Hence concentrations higher than 2% could not be attempted.

3.4 Effect of critical concentration

All these data indicate a controversial effect due to incorporation of the zinc oxide nanoparticles in the aluminium alloy sacrificial anodes. However, its role in terms of improving the metallurgical characteristics and improving the galvanic performance by means of aluminium activation are distinct. The presence of

Figure 3: The OCP decay curves of the 95-5 Al-Zn alloy sacrificial anodes reinforced with different concentration of zinc oxide nanoparticles. A: 95-5 Al-Zn, B: A + 0.1% ZnO, C: A + 0.5% ZnO, D: A +1% ZnO, E: A + 2% ZnO.
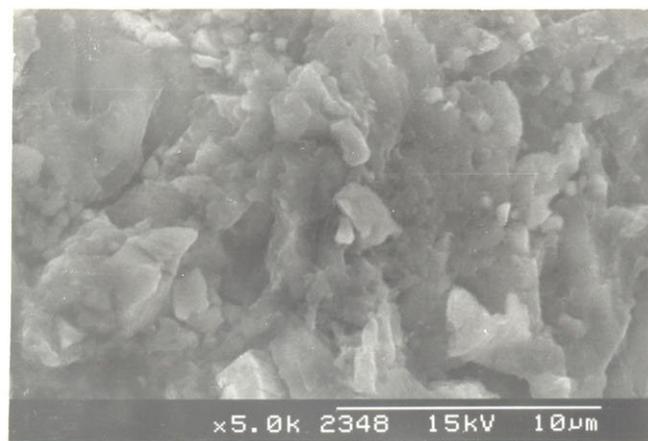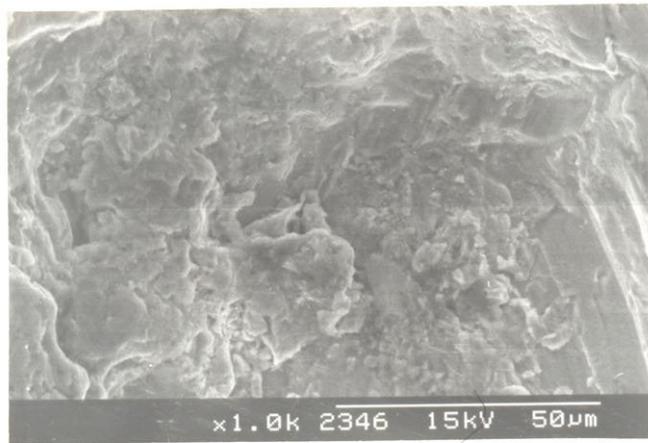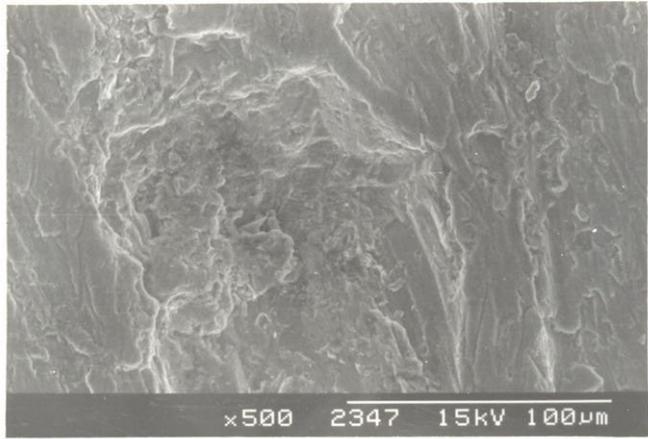
Figure 2: The SEM micrographs of the 95-5% Al-Zn alloy anodes incorporated with 1% nano zinc oxide, at different magnifications. A: x 500, B: x 1,000, C: x 5,000.
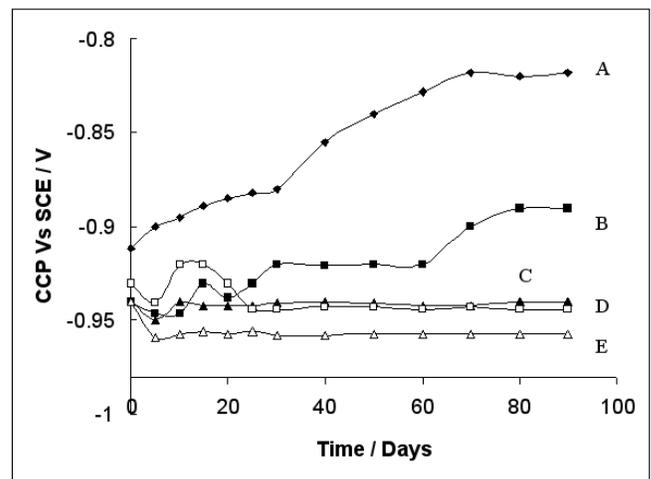
Figure 4: The CCP variation curves of the 95-5 Al-Zn alloy sacrificial anodes reinforced with different concentration of zinc oxide nanoparticles, A: 95-5 Al-Zn, B: A + 0.1% ZnO, C: A + 0.5% ZnO, D: A +1% ZnO, E: A + 2% ZnO.
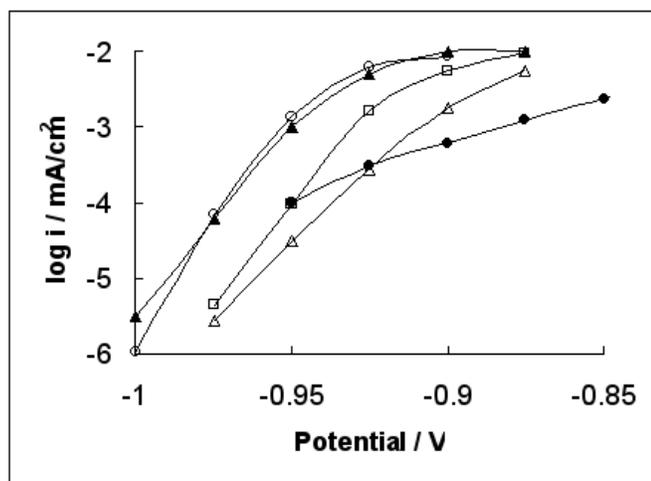
Figure 5: The anodic polarization curves of the nano zinc oxide incorporated 95-5% Al-Zn alloy sacrificial anodes. A: 95-5 Al-Zn, B: A + 0.1% ZnO, C: A + 0.5% ZnO, D: A +1% ZnO, E: A + 2% ZnO.

Table 2: Galvanic performance of Al+5% Zn alloy sacrificial anodes reinforced with different conc of nanoparticles of ZnO at an impressed current density of 0.1 mA/cm^2 (Electrolyte: 3% NaCl Solution, Cathode : Mild steel, temperature = 30^{0}C, condition : Stagnant

Anode Composition	Galvanic efficiency (%)
95/5 Al –Zn	30
95/5 Al –Zn + 0.1% ZnO	25
95/5 Al –Zn + 0.5% ZnO	28
95/5 Al –Zn + 1% ZnO	67
95/5 Al –Zn + 2% ZnO	32

nano zinc oxide efficiently activates aluminium and the effect of its concentration on the extent of activation of aluminium is not found to be a significant factor. The only limitation is that very high concentration of zinc oxide may cause heterogeneity of the alloy melt prior to casting of the anode. However, presence of the particles in the optimum concentration is crucial for obtaining significant metallurgical improvement of the anode. The presence of high concentration of zinc oxide leads to substantial reduction in self-corrosion; but is inefficient to suppress the non-columbic loss of the metal during the galvanic process, if the concentration is higher than the optimum value. Thus it become clear that keeping the optimum concentration of nano zinc oxide during reinforcing of the anode is critical to get high galvanic performance of the anode. While the effect of concentration of zinc oxide on the catalytic activation process is not significant, it is critical to improve the overall galvanic per-

formance, which is mainly depended on the extent of galvanic corrosion rather than self-corrosion.

4.   CONCLUSIONS

The zinc oxide nanoparticles prepared in the present work were suitable for reinforcing aluminium alloy anodes and were very effective in activating the sacrificial anodes. The metallurgical properties of the anodes were improved substantially by means of reinforcing the anodes with the nanoparticles, leading to a substantial reduction in the self-corrosion value. The galvanic performance of the anodes was also improved substantially by incorporating the nanoparticles in the anodes. The anode reinforced with the optimum quantity of the composite (1%) exhibited the highest over all galvanic performance. It showed very low polarization during galvanic exposure, as predicted based on the results of anodic polarization by impressed current. While the effect of concentration of zinc oxide on the catalytic activation process was not found significant, it is critical to improve the overall galvanic performance, which is mainly depended on the extent of galvanic corrosion rather than self-corrosion. Hence, incorporation of the nanoparticles in optimum quantity was found to be crucial as other combinations had negligible or even adverse effect. It should also be noted that nano zinc oxide has been reported to be bio-safe [25].

5.   ACKNOWLEDGMENTS

REFERENCES

[1] E.Y. Lyublinskii, Elektrokhimiya.9 (1973) 491.

[2] G. Qi, Z. Guo and J. Qu; Zhongguo Fusho Xu Fanghu Xuebao 21 (2001) 220. (2001) [Chem. Abs. Vol. 136, No. 92314, (200)]

[3] I. Guruppa and J.S. Karnik, Corros. Prev. and Control 43 (1996) 77.

[4] S.L. Wolfson, Mater. Perform. 33 (1994) 22.

[5] Y.M. Liou, S.C. Chung, W.J. Tsai and S.C Shih, Corros. Prev. & Control 47 (2000) 57.

[6] A. Barbucci, G. Cerisola, G. Bruzzone and A. Saccone Electrochem. Acta 42 (1997) 2369.

[7] A.R. Despic, J. Appl. Electrochem. 6 (1976) 527.

[8] A. Barbucci, G. Cerisola, and G. Bruzzone, J. alloys and Compunds 247 (1997) 210.

[9]   A. Ghosh, S. Chatterjee and B.K. Sarkar, Trans. Powder Metal. Assoc. India 26 (1999) 201.

[10] T. Kaji, H. Hattori, M. Hishikura and Y. Takeda, JP Patent 137676 (1999).

[11] T. Yamada, Y. Ogiwara and T. Doko, JP Patent 144290 (2000)

[12] M. Yan and Z. Fan, J. Mater. Sci. 36 (2001) 285.

[13] S.D. Pateves, Ceram. Inter. 22 (1996) 527.

[14] J.C. Viala, J. Bouix, G. Gonzalez and C. Esnouf, J. Mater. Sci. 32 (1997) 4559.

[15] J.P. Tu and Matsumura, Scripta. Matall. 40 (1999) 645.

[16] J.P. Tu, J. Pan, M. Matsumura and H. Fukunaga, Wear 223 (1998) 22.

[17] J.A. Yeomans and T.F. Page, J. Mater. Sci. 25 (1990) 2312.

[18] V. Laurent, D. Chatain, C. Chatillion and N. Eudthapoulas, Acta. Metal. 36 (1998) 1797.

[19] F. Hine, M. Yasuda and T. Yoshidaa, J. Electrochem. Soc. 124 (1978) 500.

[20] J. Augustynski, L. Balsenc and J. Hinden, J. Electrochem. Soc. 125 (1978) 1978.

[21] W.A. Geuard and B.C.H Steek, J. Appl. Electrochem. 8 (1978) 417.

[22] L.D. Bruke and O.J Murphy, J. Electroanal. Chem. 112 (1980) 39.

[23] B. Jabeera, Ph. D. Thesis, University of Kerala, INDIA (2002).

[24] A. Inoue, K. Nakazato, Y. Kawamura, A.P. Tsai and T. Masumoto, Mater. Trans., JIM, 35 (1994) 95.

[25] Z. L. Wang, *Materials Today* **7**, 26-33 (2004).