Materials properties of electrodeposited NiFe and NiCoFe coatings

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The codeposition behaviour of the electrodeposited iron group alloy system, NiFe and NiCoFe, was studied in acid sulphate electrolyte. X-ray diffraction measurements revealed the existence of FCC phases. X-ray fluorescence analysis of the elemental composition in NiFe and NiCoFe coatings electrodeposited over copper substrate was also carried out. The result suggested that Ni is inhibited by the presence of Fe^{2+} and Co^{2+} ions. The properties of soft magnetic NiFe and NiCoFe coatings electrodeposited in the presence of saccharin and sodium lauryl sulphate additives were studied. Corrosion performance of these coatings in 3·5% NaCl solution was evaluated using impedance electrochemical techniques. The superior coefficient of friction of NiFeCo coatings was observed from block-on ring test.

Keywords: Electrodeposition, XRD, Corrosion resistance, Wear resistance, Magnetic properties

Introduction

The iron group metals Fe, Co, Ni exhibit anomalous codeposition behaviour.[1,2] The mechanism of anomalous codeposition of iron group metals has been much studied.[3,4] In anomalous codeposition not only is the most noble species reaction rate inhibited, but the least noble metal rate is enhanced. The codeposition rate of Co, which lies between the most noble and least noble species, exhibits both features. The experience of inhibition or enhancement is concentration dependent.[5]

Electrodeposition is widely used because of advantages such as ability to control the coating composition, superior magnetic properties, control of fast deposition rate and cost effectiveness. Weihnet *et al.*[6,7] have electrodeposited a NiFe coating which is the most well known soft magnetic materials. The development of magnetic coatings has been greatly needed for many industrial areas, including magnetic induction writing heads.[8–10] High magnetic moment CoFe and NiFe are difficult to apply to practical devices because of low corrosion resistance and brittleness.[11] Oska *et al.*[12] have studied magnetic properties and other physical properties of electrodeposited NiCoFe alloys. The effect of sulphur containing additives such as saccharin and thiourea on microstructure and corrosion properties was also studied. Phan *et al.*[13] have observed that the anomalous behaviour of codeposition of NiCoFe was decreased when the solution temperature increased. A kinetic model of electrodeposition of NoCoFe thin coatings was suggested.[14–16]

Lieder and Biallozor[17] assumed the formation of $NiOH^+$ on the electrode surface and proposed that competition for surface sites between Fe^{2+} and Ni^{2+} ions resulted in the inhibition of the Ni rate. Matloz[18] proposed that metal ions are reduced in consecutive steps and the preference for high surface coverage by Fe intermediates caused inhibition of the Ni deposition. The first reduction step was of bivalent Fe^{2+} and Ni^{2+} ions to monovalent Fe^+ and Ni^+; these intermediates are adsorbed on the electrode. Yin[19] studied iron group alloy deposition and indirectly supported the two step mechanisms. Several studies have been performed to understand the effect of composition variation on the physical properties of electrodeposited NiCoFe alloy.[20–22] The recent demand for higher density magnetic storage devices requires the development of a recording head material that has a higher saturation magnetic flux density (B_s) than that of the conventional permalloy NiCo coating. Corrosion resistance of this coating has been examined in 3·5 wt-% sodium chloride solution.[23,24] The aim of the present work is to study materials properties and electrochemical corrosion resistance of these coatings.

Experimental

Mild steel substrates 72×25 mm were mechanically polished and degreased with trichloroethylene. The mild steel substrates were then electrocleaned in alkali solution containing sodium hydroxide (35 g L^{-1}) and sodium carbonate (25 g L^{-1}) for 2 min at 60°C, followed by rinsing with distilled water. Copper substrates (for XRD studies) were electrocleaned in a mild alkali solution containing sodium hydroxide (7 g L^{-1}), tri sodium orthophosphate (9 g L^{-1}) and sodium carbonate (20 g L^{-1}) for 2 min at 60°C. The substrates were finally cleaned with acetone and dried. NiFe and NiCoFe coatings of ~10 μm thick were

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Published by Maney on behalf of the Institute
Received 7 January 2009; accepted 3 August 2009
DOI 10.1179/174591909X12554332311546

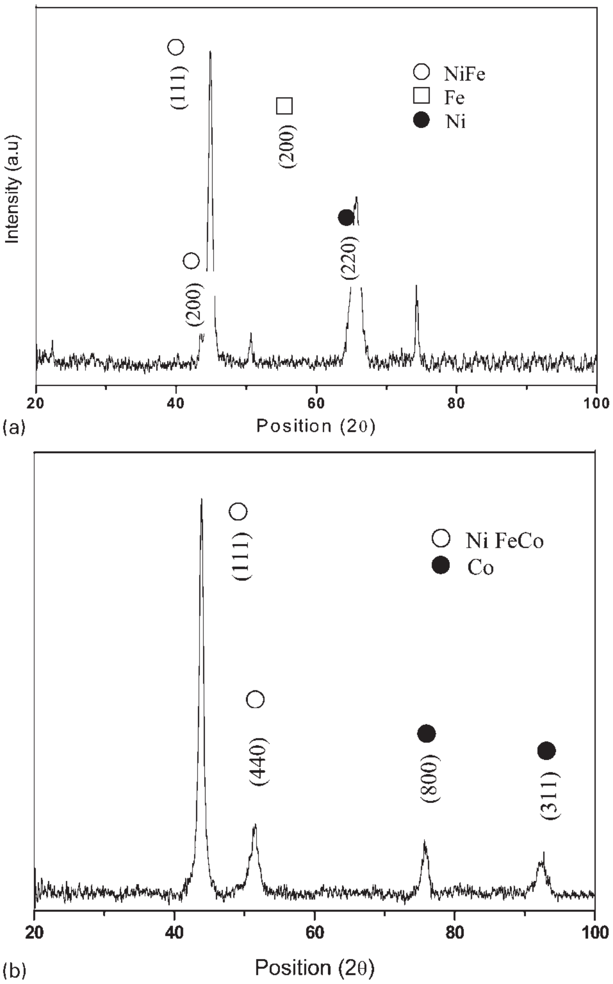
deposited over copper and mild steel substrates by using sulphate plating baths. The composition of the baths and the operating parameters for NiFe and NiCoFe electroplating are listed in Tables 1 and 2 respectively. X-ray diffraction patterns were recorded using an X'pert pro diffractometer using Cu K_α (1·541 Å) radiation from 40 kV X-ray source running at 30 mA. The composition of the coatings was analysed on a HORIBA X-ray fluorescence (XRF) spectrometer Wear resistance via coefficient of friction was measured by a block-on-ring test using as the ring material high chromium high carbon tool steel (850 HV). The magnetic properties were measured by a Lakeshore-7404 vibrating sample magnetometer with a maximum applied field of 1·5 T. Electrochemical polarisation studies were carried out using a BAS IM6 electrochemical analyser. Experiments were conducted using a standard three-electrode configuration, with a platinum foil as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the sample as the working electrode. The specimen (1·0 cm^2 exposed area) was immersed in the test solution of 3·5% NaCl. Experiments were carried out at room temperature (28°C). In order to establish the open circuit potential (OCP), before measurements the sample was immersed in the solution for ~60 min. The same three-electrode cell assembly, as used for the potentiodynamic polarisation experiments, was employed for the ac impedance investigations. The spectrum was recorded in the frequency range 10 mHz–100 kHz. The applied alternating potential had root mean square amplitude of 10 mV on the open circuit potential. After reaching the stable OCP, the upper and lower potential limits of linear sweep voltametry were set at ±200 mV with respect to OCP and the sweep rate was 1 mV s^{-1}. Tafel plots were obtained after the electrochemical impedance measurements

Table 1 Deposition parameter for electrodeposition of NiFe

Parameter	Value
Nickel sulphate, g L^{-1}	213
Ferrous sulphate, g L^{-1}	35
Boric acid, g L^{-1}	25
Saccharin, g L^{-1}	1
Sodium lauryl sulphate, g L^{-1}	0·4
pH	3–1·5
Current density, A dm^{-2}	3
Duration, min	60

Table 2 Deposition parameter for electrodeposition of NiCoFe

Parameter	Value
Nickel sulphate, g L^{-1}	56·17
Cobalt sulphate, g L^{-1}	16·8
Ferrous sulphate, g L^{-1}	3·3
Boric acid, g L^{-1}	25
Saccharin, g L^{-1}	1
Sodium lauryl sulphate, g L^{-1}	0·01
pH	2
Current density, A dm^{-2}	3
Duration, min	60



1 XRD pattern for *a* electrodeposited NiFe coating and *b* electrodeposited NiCoFe coating

Results and discussion

Phase composition

Figure 1*a* and *b* shows the XRD pattern for electrodeposition of NiFe and NiCoFe respectively on a copper based substrate. The pattern exhibits good polycrystalline structure. The comparison of *d* values calculated from the observed XRD pattern and standard *d* values from JCPDS files are shown in Table 3. It was found that there is a very good agreement in *d* values. The composition of the coatings obtained from XRF is shown in Table 4. The presence of Cu is due to the substrate, and the data indicate average composition of $Ni_{29\cdot40}Fe_{45\cdot10}Cu_{25\cdot50}$ and $Ni_{11\cdot57}Co_{55\cdot97}Fe_{32\cdot15}$ alloy.

Table 3 Comparison of *d* values from observed XRD pattern

Samples	d_{obs}	d_{std}	*hkl*	Phase
NiFe/Cu	2·015	2·013	111	NiFe
	1·805	1·767	200	NiFe
	1·244	1·249	220	Ni
NiCoFe	2·057	2·052	111	NiCoFe
	1·776	1·786	200	Ni
	1·760	1·698	440	NiCoFe
	1·241	1·201	800	Co
	1·053	1·061	931	Co

High resolution XRD measurements were carried out and showed the existence of face centred cubic (fcc) (111) and (200) peaks in the electrodeposited CoNiFe coating. The fcc phase is randomly oriented. The grain sizes were estimated with XRD from the deconvoluted fcc (111) peak by using the Scherrer formula. The grain size values for the NiFe and NiCoFe coatings were found to be 19·8 and 14·9 nm respectively. The lattice parameter of the electrodeposited coatings NiFe and NiCoFe for fcc phases is 3·550 and 3·558 Å respectively.

Corrosion resistance

The aim of this investigation is to study surface degradation resulting from electrochemical processes, thus requiring analysis of the surface deposit left after electrochemical reactions. To avoid scanning across a wide range of electrode potentials so that the surface of the material at the end of such polarisation was the result of cumulative effects at different potentials, the material was subjected to potentiostatic polarisations, one specified potential being impressed on the material at a time. The potentials were either anodic or cathodic with respect to the primary electrochemical process occurring on the surface.

The potentiodynamic polarisation curves obtained for the mild steel substrate, NiFe and NiCoFe coatings on mild steel in 3·5% *w*/*v* NaCl electrolyte are presented in Fig. 2. The current and potential of the corroding electrode is related by

$$i = i_{\text{corr}}(e^{2\cdot 3\eta/b_a} - e^{-2\cdot 3\eta/b_c}) \tag{1}$$

where i_{corr} is corrosion current, η is over potential (E–E_{corr}), b_a and b_c are anodic and cathodic Tafel slopes respectively.

At high over potentials, i.e. $\eta \gg RT/F$

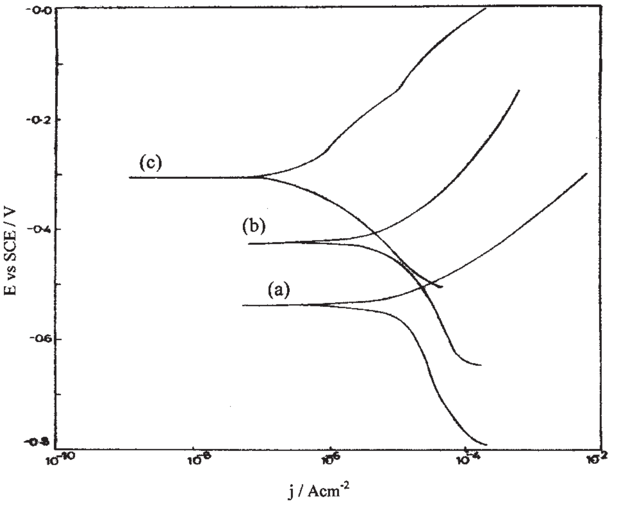
$$i = i_{\text{corr}} e^{2\cdot 3\eta/b_a}$$

$$\log i = \log i_{\text{corr}} + \eta/b_a$$

In the plot of η versus log *i*, extrapolation of the linear line to corrosion potential gives a straight line, and the slope gives both b_a and b_c and the intercept gives the corrosion current.

Table 4 Elemental composition obtained from XRF

Sample	Element	Mass%
Electrodeposited NiFe/Cu	Ni	29·40
	Fe	45·10
	Cu	25·50
Electrodeposited NiCoFe/Cu	Ni	11·87
	Co	55·97
	Fe	32·15



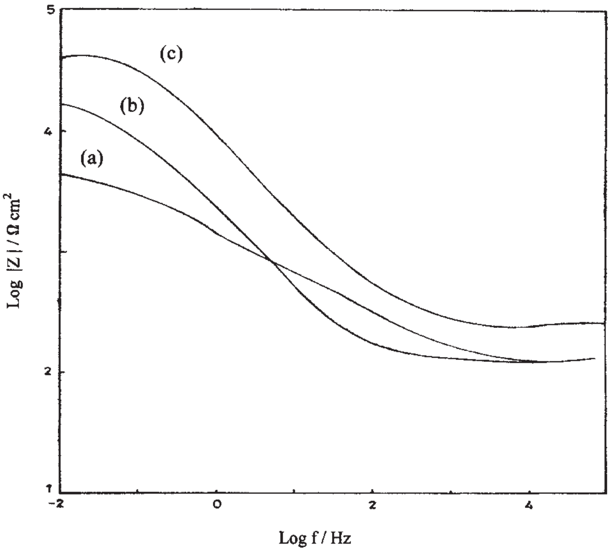
2 **Polarisation curve obtained for *a* pure mild steel, *b* NiFe over mild steel and *c* NiCoFe over mild steel in 3·5 wt-% NaCl**

The E_{corr} and I_{corr} values have been calculated using the Tafel extrapolation method and are given in Table 5. There is an appreciable increase in corrosion resistance for the NiCoFe alloy deposit on the mild steel substrate compared to NiFe on mild steel and bare mild steel substrate. E_{corr} and I_{corr} values improve (a less negative value of E_{corr} and lower value of I_{corr} signifies an improvement in corrosion) for NiCoFe on mild steel substrate. For the NiCoFe coating on mild steel, the corrosion current is observed to be the lowest, $0\cdot003 \times 10^{-5}$ A cm^{-2}, as indicated in Table 5. The corrosion current is as high as $1\cdot17 \times 10^{-5}$ A cm^{-2} for the NiFe layer on steel in which the rapid corrosion of iron takes place at the cavities of the coating owing to the combined effect of the rather noble steady state potential of the NiFe coating and the relatively active iron species. Consequently, the corrosion of mild steel is accelerated in spite of the NiFe coating.

The Bode plots for the samples used for corrosion tests in 3·5% *w*/*v* NaCl solution are shown in Fig. 3. When the sample is immersed in the electrolyte the defects in the coating provide the direct diffusion path for the corrosive media. In this process galvanic corrosion cells are formed and the localised corrosion dominates the corrosion process. Table 6 gives the values of charge transfer resistance R_{ct} and the double layer capacitance C_{dl}. The measured R_{ct} of the NiCoFe sample was the highest at 811·9 Ω cm^2 and, consequently, the double layer capacitance would be at a minimum for this deposit,; it was found to be $2\cdot6 \times 10^{-3}$ F cm^{-2}.

Table 5 Corrosion parameters obtained from polarisation studies in 3·5% NaCl (*w*/*v*)

	Tafel slope, V/decade				
Sample	E_{corr}, mV(SCE)	b_a, mV/decade	b_c, mV/decade	I_{corr}, $\times 10^{-5}$ A cm^{-2}	Corrosion rate, $\times 10^{-3}$ mpy
Pure mild steel	−538	87	357	1·55	71·0
NiFe on mild steel	−425	151	235	1·17	23·1
NiCoFe on mild steel	−308	119	97	0·003	1·6



3 **Bode plot obtained for *a* pure mild steel, *b* NiFe over mild steel and *c* NiCoFe over mild steel**

Wear resistance

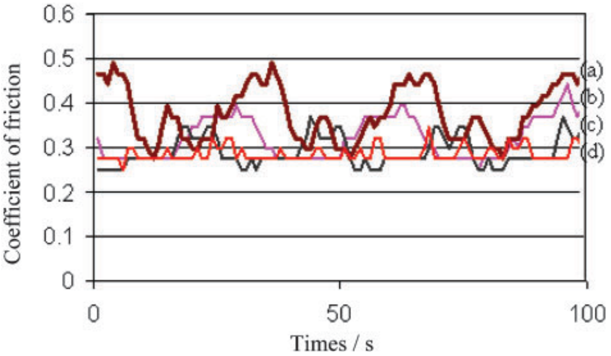
The ring material used for the block-on-ring rest is high chromium carbon tool steel (850 HV). NiFe and NiCoFe coatings on mild steel have higher wear resistance than mild steel due to the low coefficient of friction shown by the alloy coatings. Figure 4 presents the coefficient of friction shown with the steel sliding against NiFe and NiCoFe, nickel electroplate and mild steel. Figure 4 shows that the coefficient of friction is minimum for NiCoFe coatings on mild steel.

Magnetic properties

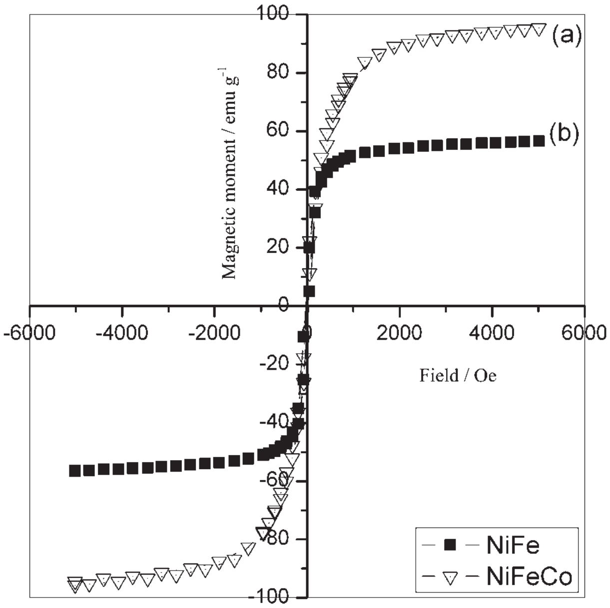
Soft magnetic NiFe and NiFeCo thin films with high magnetic saturation and low coercivity have been successfully prepared by the electroplating method. The magnetisation loops (M–H loop) of NiFe and NiFeCo[25] thin films were prepared by electrodeposition of the alloys on mild steel substrate as described above. NiFe thin films exhibited a maximum coercivity of 23 Oe with an M_s of 54 emu g^{-1} (Fig. 5*a*). Figure 5*b* shows the enhancement of magnetic saturation M_s which was observed for the NiFeCo thin film. More than one and half times increase in M_s was observed for the NiFeCo thin films; this could be due to development of crystalline anisotropy and freedom from surface oxidation.[26] The magnetic properties of NiFeCo ($Ni_{11\cdot 57}Co_{55\cdot 97}Fe_{32\cdot 15}$ composition in this study) thin film possessed a maximum coercivity of 12 Oe with an M_s of 94 emu g^{-1} as shown in Fig. 5*b*. A drastic change in the intrinsic magnetic property of the NiFeCo thin films was obtained by this electrodeposition method and the reported values were comparable with the reported data on $Co_{50}Ni_{10}Fe_{40}$ alloy obtained by Dinesh *et al.*[27] The results are also in broad agreement with data reported by Tang[28] from an earlier study in which a periodic reverse pulse electrodeposited $Ni_{18\cdot 1}C_{58\cdot 5}Fe_{23\cdot 4}$ alloy showed a coercivity value of just over 6 Oe.

Table 6 **Corrosion parameter obtained from impedance measurements (Bode plot)**

Sample	R_{ct}, Ω cm²	C_{dl}, ×10⁻³ F cm⁻²
Pure mild steel	442·8	6·3
NiFe on mild steel	517·3	2·7
NiCoFe on mild steel	811·9	2·6



4 **Coefficient of friction curve for *a* mild steel substrate, *b* Ni, *c* NiFe and *d* NiCoFe**



a NiFe thin films; *b* NiFeCo thin films

5 **Hysteresis curve of soft magnetic thin films prepared by electrodeposition on mild steel**

Conclusions

NiFe and NiCoFe coatings of 10 μm thick were codeposited successfully in acid sulphate electrolyte. A good polycrystalline nature with an fcc structure was observed from XRD studies. The NiCoFe coating possesses fcc structure with orientation along (111) and (200) planes. Soft magnetic nature was observed from vibrating sample magnetometer studies. The enhancement of magnetic saturation M_s was observed for the NiFeCo thin film over that of the NiFe alloy. The value of the charge transfer resistance was found to be the highest for the ternary deposit. Block-on-ring tests showed that the coefficient of friction is minimum for NiCoFe coatings on mild steel.

References

1. A. Brenner: 'Electrodeposition of alloy', Vol. 1–2; 1963, New York, Academic press.

2. N. H. Phan, M. Schwartz and K. Nobe: *J. Appl. Electrochem.*, 1991, **21**, 672.
3. N. H. Phan, M. Schwartz and K. Nobe: *J. Electrochem. Acta*, 1994, **30**, 449.
4. Y. Zhuang and E. J. Podlaha: *J. Electrochem. Soc.*, 2000, **147**, 2231.
5. Y. Zhuang and E. J. Podlaha: *J. Electrochem. Soc.*, 2002, **150**, 800.
6. Y. Weihnet, L. Peter, J. Tolk, J. Padar, Z. Kerner, C. M. Schnerder and I. Baskonyi: *J. Electrochem. Soc.*, 2003, **150**, C507.
7. S. Leopold, M. Herranen and J. O. corlsson: *J. Electrochem. Soc.*, 2001, **148**, C507.
8. P. C. Andricacos and N. Robertson: *IBM J. Res. Develop.*, 1998, **42**, 671.
9. E. I. Cooper, C. C. Bonhote, J. Heidmann, Y. Ksu, P. Kern, J. W. Lam, M. Ramasubrmanian, N. Robertson, L. T. Romankiw and H. Xu: *IBM J. Res. Develop.*, 2005, **49**, 103.
10. E. Gonez, E. Pellicer and E. Vallas: *Electrochem. Commun.*, 2005, **7**, 275.
11. B. D. Cullity: 'Introduction to magnetic materials', 529; 1972, Reading, MA, Addison-Wesley.
12. T. Oska, M. Takai, Y. Sogawa, T. Momma, K. Dhsashi. M. Satto and K. Yamada: *J. Electrochem. Soc.*, 1999, **146**, 2092.
13. N. H. Phan, M. Schwartz and K. Nobe: *J. Appl. Electrochem.*, 1991, **21**, 672.
14. Y. Zhuang and E. J. Podlaha: *J. Electrochem. Soc.*, 2000, **147**, C231.
15. Y. Zhuang and E. J. Podlaha: *J. Electrochem. Soc.*, 2003, **150**, C219.
16. Y. Zhuang and E. J. Podlaha: *J. Electrochem. Soc.*, 2003, **150**, C225.
17. M. Lieder and S. Biallowor: *Surf. Technol.*, 1985, **26**, 23.
18. M. Maltosz: *J. Electrochem. Soc.*, 1993, **140**, 2272.
19. K. M. Yin: *J. Electrochem. Soc.*, 2003,**150**, C435.
20. J. Gong, W. H. Butler and G. Zangari: *Appl. Phys. Lett.*, 2005, **87**, 012505.
21. T. Osaka, M. Takai, K. Hayassi, Y. Sogawa, K. Ohashi, Y. Yasue, M. Saito and K. Yamada: *IEEE Trans. Magn.*, 1998, **34**, 1432.
22. B. Y. Yoo, S. C. Hernandez, D. Y. Park and N. V. Myung: *Electrochim. Acta*, 2006, **51**, 6346.
23. N. Ishiwata, C. Wakabayashi and H. Urai: *J. Appl. Phys.*, 1991, **69**, 5616.
24. Y. K. Kim, H. Y. Son, Y. S. Choi, K. Moon and K. H. Sunivoo: *J. Appl. Phys.*, 2000, **87**, 5413.
25. F. M. F. Rhen and S. Roy: *J. Appl. Phys.*, 2008, **103**, 103901.
26. A. H. Chandra Mishra, T. Sahoo, V. Srinivas and A. K. Thakur: *J. Alloys Compd*, 2009, **480**, 771.
27. D. K. Pandya, Y. Kumar, S. C. Kashyap and S. Chaudhary: *Int. J. Nanosci.*, 2006, **5**, 605.
28. P. T Tang: *Trans. IMF*, 2007, **85**, (1), 51–56.