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Study on synthesis of magnetic nanocomposite (Ni-Teflon) by swift heavy ion beam mixing

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ABSTRACT

The present work envisages synthesis of magnetic nanocomposites by ion beam mixing technique using swift heavy ion irradiation of Ni-Teflon bilayer system and its magnetic characterizations. The nanocomposite is characterized by Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM), scanning probe microscopy (SPM) and superconducting quantum interference device (SQUID) magnetometer. Cross-sectional TEM and magnetic force microscopy (MFM) results confirm the formation of nanocomposite. Magnetic characterizations reveal that nanocomposite exhibits ferromagnetic behavior with an increase in the coercivity, which is attributed to the formation of Ni nanoparticles. The coercivity of the nanocomposite is found to be 112 Oe at room temperature which is two orders of magnitude larger than that of the bulk Ni (0.87 Oe).

Keywords: Ion beam mixing; swift heavy ions; metal-polymer nanocomposite; magnetic properties.

Jai Prakash received his masters degree in Chemistry from the Ch. Charan Singh University (C. C. S. Univ.), Meerut, India. He is registered for Ph. D in Chemistry from C. C. S. University and working on the project entitled 'Study of swift heavy ion induced mixing in metal-polymer systems', funded by Inter University Accelerator Centre (IUAC), New Delhi. His current fields of interest are synthesis and study of polymer based nanocomposites by ion beam irradiation.

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Introduction

Metal nanoparticles dispersed in insulating polymeric matrices have been a subject of great interest in area of thin film device application and fabrication of nanoelectronics devices. Incorporation of nanoparticles into a polymeric system may impart novel magnetic, semiconducting or optical properties, depending on the kind of nanoparticles and their characteristics formed in the system. The magnetic nanocomposites possess unusual properties such as giant magneto resistive effect [**1, 2**] and hence have potential application in super high-density data storage devices [**3-5**]. Such encapsulated particles can be used in magnetic recording media in tape or disc form, can be used as moldable magnetic powders in electro photography [**6**, **7**] and in diagnostic medical tools e.g. for magnetic resonance tomography, magnetic resonance imaging etc. [**8**, **9**]. The applicability of these nanocomposites can be considerably improved by tuning their conventional magnetic characteristics such as saturation magnetization, coercive force etc. [**10**].

Several reports exist in literature on the synthesis of metal polymer nanocomposites with magnetic particles of Fe, Co and Ni using different methods [**11-15**]. Ionizing irradiation (i.e., e^- or ions) is a promising method for the synthesis and engineering of nanostructures either on the surface [**16**] or embedded in a matrix [**17**, **18**]. Ion implantation is one of the specific techniques used to implant controlled metal nanoparticles for synthesizing nanocomposites**.** It provides a versatile method for controlling the concentration and depth profile of doping elements [**19**, **20**]. However, low concentration and depth inhomogeneity of implanted ions are the major limitations of ion implantation technique [**21**]. Ion beam mixing (IBM) is an alternate method by which doping with high concentration can be achieved by ion irradiation of a thin metal film grown on the desired matrix with much lower doses. IBM in ballistic regime is limited to the range of defects when the elements are insoluble at equilibrium. It is extended up to the range of primary recoils in experiments with heavy ions of a few MeV as reported by Rizza et al. [**21**] and Pivin et al. [**22**]. They have reported the fragmentation of noble metal layers in nanoclusters by a process of mixing using 3-4.5 MeV Au ion followed by reprecipitation. Extension of the concept of IBM to the regime of electronic stopping using swift heavy ion (SHI) is not straight forward and only a few experiments have been performed [**23**]. However, the mixing by diffusion in fluid phases which occurs in purely electronic stopping regime of ion slowing down where local transient target heating exceeds the melting or boiling point, is attractive [**24**] and many studies on SHI induced interface mixing have been reported by co-authors [**24-26**]. But until now few attempts have been made to mix the insoluble phases by this process [**21**].

Polymers having low dielectric constant are attractive materials for the synthesis of nanocomposites [**27**]. Among them, Teflon is a particularly suitable choice for microelectronic devices because of its chemical inertness, high thermal stability and low dielectric constant (~2.0). In the present study, we report on application of IBM in electronic energy loss regime for preparing magnetic composite of Ni nanoparticles embedded in carbon rich Teflon matrix using 120 MeV Au ions.

Experimental

Samples were prepared by e-beam evaporation of Ni on Teflon [PTFE = Polytetrafluoroethylene] substrate (thickness ~ 1 mm) in high vacuum deposition chamber (at a base pressure of ~10^{-7} torr). The deposition rate was 0.4-0.5 Å/s and film thickness was 100 nm as measured using a quartz crystal thickness monitor. The ion beam irradiation was carried out with 120 MeV Au ions produced by 15 MV Pelletron accelerators at Inter University Accelerator Centre (IUAC), New Delhi, India. More details of the sample preparation and ion irradiation parameters (i.e., energy losses and penetration depth of the Au ions etc.) are reported in our previous publication [**28**]. Rutherford backscattering spectrometry (RBS) was performed using 2 MeV He^+ ions at the scattering angle of 160° at Institute of Physics (IOP), Bhubaneswar, India. Atomic force microscopy (AFM) and magnetic force microscopy (MFM) images were taken in tapping mode at the room temperature using NanoScope IIIa SPM at IUAC, New Delhi. MFM measurements were performed at the different lift heights before and after irradiation without any applied magnetic field. An antimony doped silicon tip coated with magnetic layer of Co/Cr was used. Magnetization measurements were carried out using superconducting quantum interference device (SQUID) magnetometer in the dc mode with Quantum Design MPMS-XL magnetometer at IIT Roorkee and in plane measurement data was recorded at different temperatures. Coercivity of the samples was measured by recording magnetization versus applied field hysteresis loops at different temperatures. Cross-sectional transmission electron microscopy (X-TEM) was performed for the size estimation of Ni nanoclusters using JEOL, JEM-2100F operated at 200 keV at Inha University, Incheon, South Korea.

Results and discussion

The thickness of deposited Ni film was determined by RBS measurement and was found to be ~ 100 nm using Rutherford universal manipulation program (RUMP) simulation code [**29**]. RBS spectra of the Ni-Teflon pristine sample and sample irradiated with 120 MeV Au ions at the fluence of 5×10^{13} ions/cm^2 have earlier been shown in Ref. 28. Their comparison evidences strong mixing in the Ni-Teflon system after irradiation. Moreover, mixing was further evidenced by the presence of F (on the surface) and the formation of NiF_2 compound (on the surface and in-depth) in the irradiated sample as confirmed by electron spectroscopy for chemical analysis (ESCA)**.** The mixing is explained by the chemical reactions of Ni and reactive polymer species within the molten ion tracks in the Teflon and hot zones around the ion paths in Ni film due to electronic energy loss induced by 120 MeV Au ions [**28**].

In order to understand the nature of intermixing and to estimate the particle size, X-TEM was carried out on ion irradiated sample. **Fig. 1 (a)** shows the X-TEM image and corresponding selected area electron diffraction (SAED) pattern of the Ni-Teflon sample irradiated with 120 MeV Au ions at the fluence 5×10^{13} ions/cm^2. It shows the

formation of Ni nanoclusters of irregular size and shape embedded in carbon enriched polymer matrix as also shown in magnified X-TEM images [**Fig. 1 (b-c)**]. Carbon rich cylinders are formed due to evolution of fluorocarbon gases from the Teflon on ion irradiation [**28**]. SAED pattern [inset **Fig. 1 (a)**], taken from the irradiated sample, shows the number of diffraction rings with bright spots which may be attributed to the polycrystalline nature of the Ni nanoclusters. Besides X-TEM measurements which show the formation of nanocomposite the, atomic force microscopy (AFM) was also performed to study the nanoclusters present on the surface.

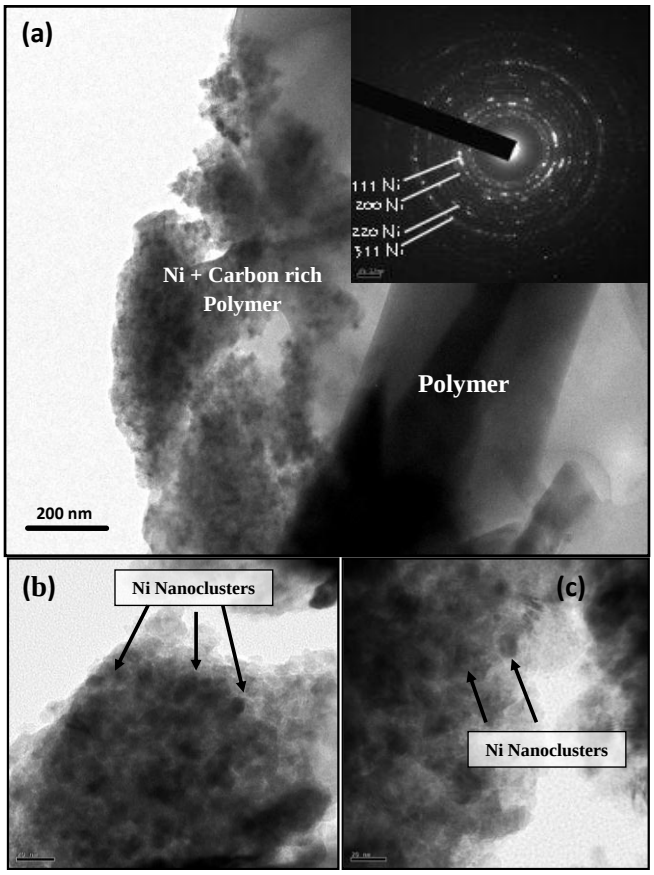

Fig. 1. (a) Cross sectional transmission electron microscopy (X-TEM) image with selected area electron diffraction (SAED) pattern (inset) of irradiated Ni-Teflon sample with 120 MeV Au ions at the fluence 5×10^{13} ions/cm^2. (b) and (c) The magnified X-TEM images show the Ni nanostructures of irregular size and shape embedded in carboneous matrix. X-TEM images reveal the formation of Ni-Teflon nanocomposite and corresponding SAED image shows the polycrystalline nature of Ni nanoclusters.

In order to study the magnetic properties of nanocomposite, magnetic domain structures along with the surface topography of the Ni-Teflon samples before and after irradiation were imaged in tapping mode. The 2 μm × 2 μm AFM and the corresponding MFM images (a) before and (b) after irradiation are shown in **Fig. 2**. The phase images were studied at different lift heights and the lift height for MFM measurement was kept at 40 nm after ensuring that the phase image does not have contribution from topographic features. The AFM image shows the formation of clusters after irradiation, whereas MFM image shows the strong magnetic nature of these clusters.

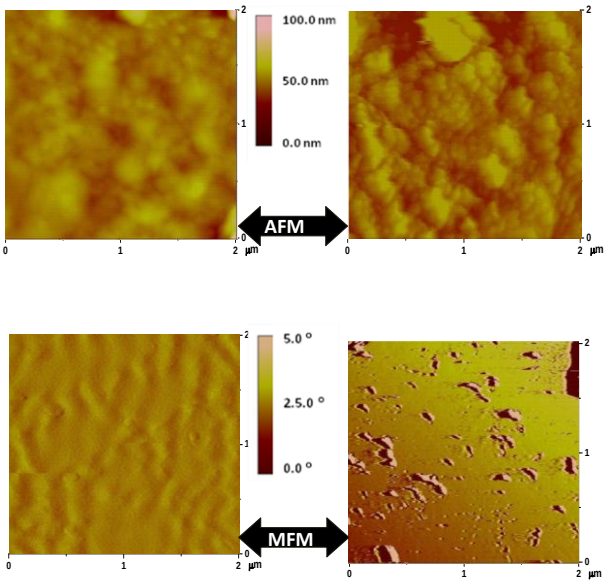

Fig. 2. AFM and MFM images (2 × 2 μm) of Ni-Teflon sample (a) before and (b) after irradiation with 120 MeV Au ions at the fluence 5×10^{13} ions/cm^2. Measurements are done with zero applied magnetic field at the room temperature. Both the AFM and the MFM images are displayed with the same Z scale of 100 nm and 5° respectively. MFM measurements were carried out at a lift height 40 nm to remove the effect of topographic features from the phase image.

Magnetic properties were further studied using SQUID magnetometer and magnetization versus applied magnetic field (M-H) curves were recorded at 5, 100 and 300 K for the Ni-Teflon pristine, irradiated and annealed (after irradiation) samples as shown in **Fig. 3**. It should be noted that no correction has been made in SQUID raw data due to the diamagnetic contribution from the substrate (Teflon) during the measurement. The hysteresis curves are typical of ferromagnetism in nature and the saturation magnetization is not changing with temperature for the irradiated sample. The material is still ferromagnetic after irradiation but the saturation magnetization decreases by a factor of 10 [**Fig. 3 (a, b)**]. The magnetization saturates above 600 Oe and magnetization values are ~11.6 and ~ 0.9 emu/g (assuming the density of the bulk material) for the pristine and irradiated samples respectively, whereas for bulk Ni, it is 58.5 emu/g [**30**, **31**]. The low saturation magnetization value as observed for the pristine film may be due to oxygen contamination at the surface, facilitated by the nanometric size of Ni grains or to some interfacial reaction of Ni with F of the Teflon. This value is further decreased on irradiation and it may be due to the formation of NiF_2 [**25**], as the resulting NiF_2 phase is known to be antiferromagnetic in nature [**32**]. The coercive field values (H_c) noted from the M-H curves of pristine film are 272, 189, 60 Oe and after irradiation these are found to be 248, 200, 112 Oe at 5, 100, 300 K respectively. Kumar et al. [**3**] have reported a similar response of coercivity with increase in temperature, in case of Ni nanoparticles embedded in TiN matrix. Here, it should be noted that after irradiation, the coercivity of the nanocomposite tends to increase at high temperature as compared to the pristine sample. In addition, the H_c value found at room temperature (RT) for

irradiated sample (nanocomposite) is approximately two orders of magnitude larger than that of pure Ni (0.87 Oe) **[30].**

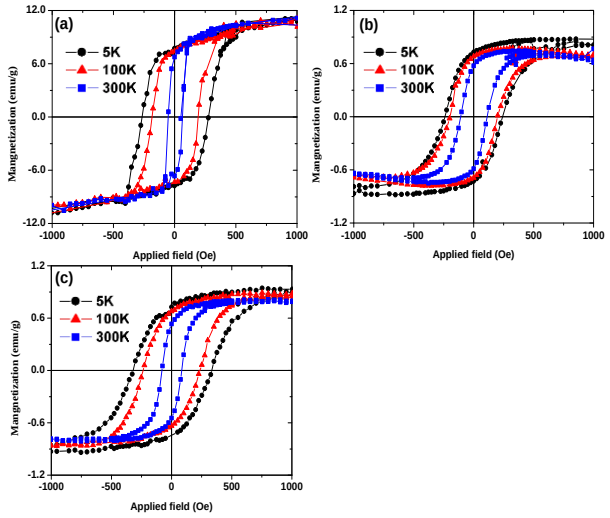

Fig. 3. Magnetization versus applied magnetic field (M-H) curves for Ni-Teflon samples at 5, 100 and 300 K for (a) pristine sample (b) sample irradiated with 120 MeV Au ions at the fluence 5×10^{13} ions/cm^2 and (c) irradiated Ni-Teflon sample after annealing for 1 hour at 100 °C. No correction has been made in the SQUID raw data due to diamagnetic contribution from the Teflon substrate in any case.

Table 1. The coercive field (H_c) values for pristine, irradiated and annealed samples at different temperatures.

	Coercivity (Oe)		
Temperature (K)	Pristine Ni-Teflon	Irradiated Ni-Teflon	Irradiated + annealed at 100 °C
5	272	248	326
100	189	200	238
300 (RT)	60	112	85

The coercivity of magnetic particles is known to be particle size dependent [**30**, **31**, **33**]. Sekino et al. [**31**] have reported a similar observation on increase in coercivity (~40 Oe) for Ni-Al_2O_3 nanocomposite at RT and attributed it to the dispersion of Ni nanoparticles in Al_2O_3 matrix. Kim et al., [**30**] have reported that the two orders of magnitude high coercivity of Ni-Al_2O_3 nanocomposite as compared to pure Ni, is due to the magnetic single domain structure of Ni nanoparticles. The irradiated sample was further investigated to see the effect of annealing and sample was annealed at 100 ºC for 1 hour. **Fig. 3 (c)** shows that after annealing, the material is still ferromagnetic with a saturation magnetization of same order of magnitude with increase in coercive field measured at 5 and 100 K. But the coercive field decreases with respect to irradiated sample when measured at RT as shown in **Table 1**. The reason for these high coercivities is most probably the instability of domain walls which otherwise facilitate the spin rotation in soft magnets like Ni. It should be noted that, the largest coercivity is measured when a single magnetic domain structure is formed [**33**], though we have no proof of the same in present study. These Ni nanoparticles have size undoubtedly below the ferro to paramagnetic transition value at RT and show a ferromagnetic behavior in the irradiated sample. When annealed, their mean size seems to increase and hence coercive field decreases.

Conclusion

Synthesis of Ni-Teflon nanocomposite using swift heavy ion irradiation of thin Ni film deposited on Teflon and its magnetic characterization, have been reported. Ni nanoclusters are formed in carbon rich polymer matrix due to the effect of irradiation. M-H curves show a ferromagnetic behavior for the nanocomposite with an increase in coercivity at room temperature. The present work demonstrates that swift heavy ion induced mixing can be used as a tool to synthesize magnetic nanocomposites.

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