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Rapidly quenched magnetic materials for functional and sensor applications

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Abstract : Rapidly quenched (RQ) amorphous / nanostructured materials have been addressed in relation to their properties targeted towards potential applications. Quenching techniques like melt spinning and in-water quenching for production of these materials in the form of ribbons and microwires production respectively have been addressed. CoFe-based microwires exhibited interesting giant magneto-impedance (GMI) behviour and was used in development of GMI sensor for detection of carburization in austenitic stainless steel. Efforts have been laid on the production of Fe-based magnetostrictive amorphous ribbons and their potential use in magnetostrictive sensor (MsS) for generation of guided waves for detection of defects in pipes. Compositional tailoring has also been carried out in amorphous / nanostructured ribbons to raise the saturation magnetization beyond 1.6 Tesla. Some of these ribbons have also been found to manifest interesting electromagnetic interference shielding effectiveness (EMI SE) properties.

Keywords: *Rapid quenching, magnetic, amorphous, nanostructured, giant magneto-impedance (GMI), electromagnetic interference shielding effectiveness (EMI SE).*

INTRODUCTION

In recent years, there has been a paradigm shift in the materials development strategies. Such approaches circumscribe not only the aspects of fundamental studies but also their potentiality towards applications. Amongst such materials, the advanced magnetic alloys have drawn special attention due to emerging synergy between properties and application requirements. The properties of these ferromagnetic materials can be tailored through different non-conventional processing routes. Amongst different processing methodologies, the rapid solidification is a potential route to get amorphous / nanostructured metallic precursors directly from the melt [1] and thereby reducing magnetic anisotropy energy in a greater extent than the crystalline counterpart. In this route, melt spinning to get ribbons /foils [2] or in-water quenching to get microwires [3,4] are some of the prevalent techniques. These techniques for getting metastable materials have an edge over the others in view of their efficiency in producing materials in large scale. The property of as-prepared precursors can be modified through control of alloy chemistry, rapid solidification parameters and heat treatment schedule. The modification in the processing conditions can deliver desired intrinsic and extrinsic magnetic properties. Bench marked properties pertaining to saturation magnetisation, saturation magnetostriction, Curie temperature, coercivity, permeability and coreloss are some of the targeted ones. Till the advent of metastable materials, these properties were catered by conventional crystalline materials. The metastable amorphous/nanostructured magnetic alloys find applications in distribution transformers [5], electrical components for electric vehicles (EVs)[6] etc. In these applications, the amorphous / nanostructured materials exhibit excellent performance due to their low coreloss and high permeability [7]. In the application areas of distribution transformer, these new materials are competing against conventionally known silicon steels like cold rolled grain oriented (CRGO) and non-oriented (CRNO) ones due to their reduced coreloss. However, the limiting scope of amorphous materials due to their lower induction values has been taken as a challenge worldwide to push their restricting limits of saturation magnetisation through appropriate tailoring of compositions [8,9].

The scope of metastable magnetic materials is further widened due to their potentiality as elements in sensors for structural health monitoring (SHM) of industrial components which are predominantly made of ferromagnetic

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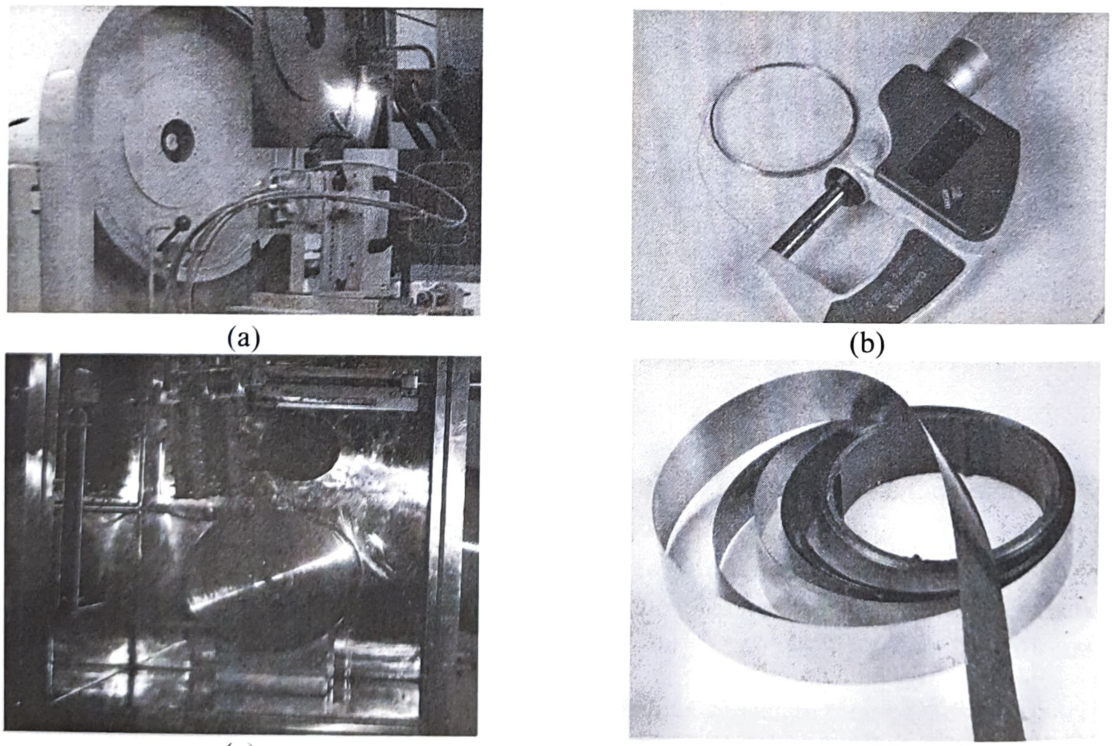
steel. The typical magnetic sensing devices for SHM have been developed on the principle of magnetostrictive sensors (MsS)[10,11], giant magnetoimpedance sensors (GMI) [12], fluxgate magnetometer [13] etc. The low driving field requirements for magnetostriction in amorphous materials is an appealing parameter in sensor and transducer design concepts. The amorphous / nanostructured based MsS sensors are under current research priority in our laboratory for their scope in SHM through generation of ultrasonic guided waves and consequent detection of defects in components like pipes [14] and plates. Apart from magnetostriction, the amorphous materials also display sensitive change in magneto-impedance (MI) even at feeble external magnetising field. In view of sensitivity in very low magnetic field, the GMI based materials [15] and sensors are being explored for detection of phase transformation in steels. With increasing application of amorphous and nanostructured magnetic materials for sensors, attempts have been made in recent years of using these materials for electromagnetic interference (EMI) shielding elements. The EMI shielding or absorption materials are key to avoid the signal/noise interference, device malfunctioning and electromagnetic pollution to humans. The EMI shielding materials are typically composite structures using dielectric and/or magnetic filler materials to attenuate the incoming electromagnetic waves [16]. Recently, shielding through absorption is highly desirable for their stealth and environmental benefits.

The present investigation is focussed on development of various metastable magnetic materials and their desirable functional properties for different applications. The issues related to compositional tailoring, process control and sensing applications have been addressed in this paper.

RAPID QUENCHING OF MAGNETIC ALLOYS

The alloys in the form of ribbons / foils and wires that have been used in the present study have been developed in our laboratory through rapid quenching techniques. Prior to quenching, the master alloys are prepared through arc melting of pure elements under inert atmosphere. A series of Fe-, CoFe- and Co-based alloys have been prepared with different stoichiometric variation.



(a) (b) (c) (d)

Fig. 1. Photographs of (a) In-water quenching system (inset: melt ejection) and (b) amorphous wires, (c) melt spinning system and (d) melt spun ribbon.

In these wires, the ferromagnetic elements of Co, Fe contribute towards magnetic components while the metalloids (Si, B) are the stabilizers for the glassy phase. The thermally stable refractory element Nb acts as a grain growth retarder to inhibit nucleation and growth phenomena of crystallites. The amorphous / nanostructured metallic microwires have been processed through in-water quenching apparatus (Fig-1a). The alloy was re-melted and ejected (Fig-1b) through quartz crucible orifice into the rotating water drum of this apparatus to get continuous microwires with diameter in the range of 80 to 120 microns. Argon pressure of 3-4 bar was maintained for ejection of alloy melt into drum rotating at speed of 300 – 350 rpm. Similarly, the amorphous / nanostructured ribbons have been prepared using a melt spinning system (Fig-1c) with a quenching wheel made of oxygen free copper. The master alloy is induction melted and ejected through a slit orifice in the bottom of the quartz crucible to get ribbons (Fig-1d) upto 25mm width and thickness of around 25 to 35 microns.

GIANT MAGNETO-IMPEDANCE BEHAVIOR IN MICROWIRES AND SENSOR APPLICATION

The giant magneto-impedance is a phenomenon wherein the amorphous wires / ribbons reveal a large change in ac complex impedance with applied dc magnetic field in the presence of a small alternative current applied on the material[17]. The property is evaluated in terms of percentage change in magneto-impedance with respect to a maximum applied dc magnetizing field. The magneto-impedance of the prepared microwires was measured using an impedance analyser (Agilent 4294A) through four probe technique wherein the applied ac current and frequency are optimized to achieve maximum GMI ratio. Typical GMI plots of representative amorphous microwires are shown in Fig-2. It is observed that the incorporation of thermally stable Nb in

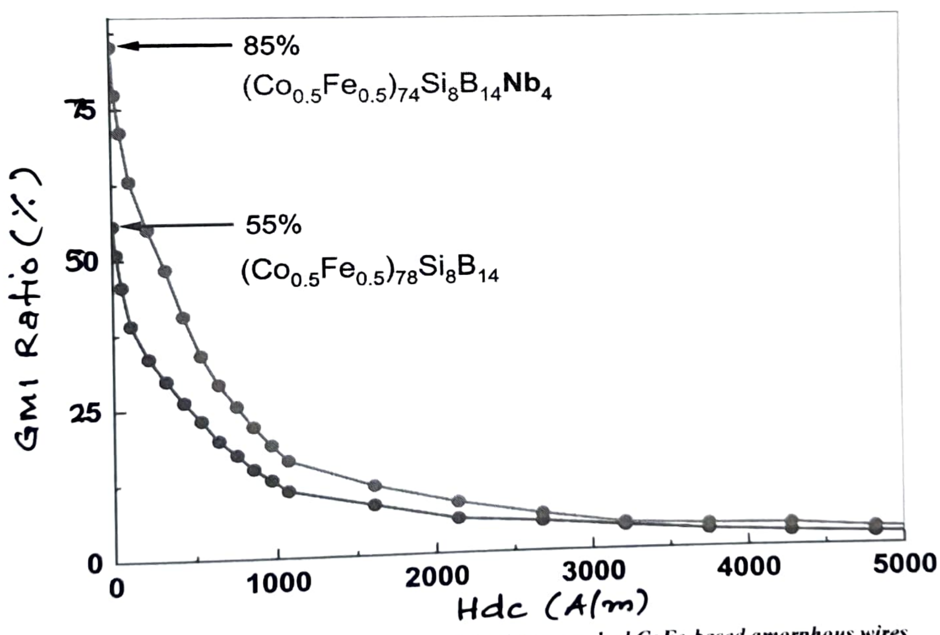
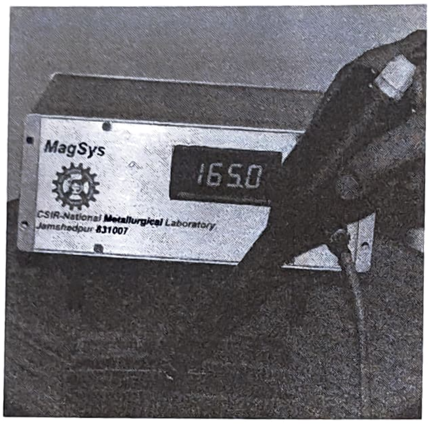


Fig.2. Giant magneto-impedance plots of as-quenched CoFe-based amorphous wires

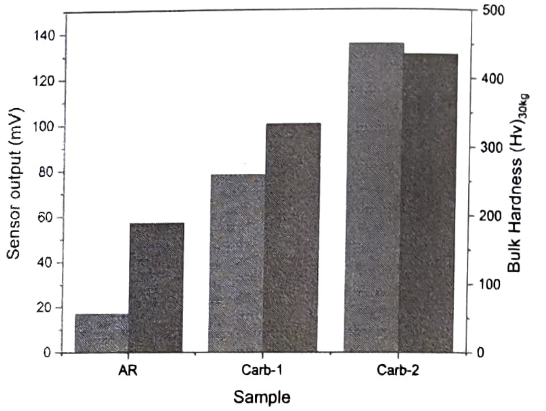
CoFeSiB system (with Co:Fe :: 50:50) enhanced the GMI_{max} value from 55% to 85%. GMI values were obtained (Table-1) for a series of microwires with incorporation of Cr and also with stoichiometric variation of Co / Fe ratio. It was observed that optimal content of Cr along with appropriate tailoring of ferromagnetic constituents like Co and Fe further improved the GMI properties. The microwire with high GMI_{max} values was used as a sensing core element inside the probe of a Giant magneto-impedance based device. The sensing device (Fig-3a) developed in the laboratory using above mentioned microwires was able to detect the effects of carburization in a Ti-stabilized austenitic stainless steel (SS321). This type of problem is faced by petroleum refining industry where cracking of hydrocarbon takes place in a reactor unit made of SS321. The sensor output voltage for three samples with varied carburization level (industrially carburized and heat treated) are shown in Fig-3b. AR represents the sample which was not carburized. Other samples were and subsequently heat treated at 800°C for one hour (Carb-1) and 12 hours (Carb-1) for carbide precipitation. The carburized sample also showed increase in mechanical hardness with soaking time.

Table-1 : GMI_{max} (%) values for CoFe-based amorphous microwires

Alloy Composition (at%)	GMI_{max} (%)
$(Co_{0.5}Fe_{0.5})_{78}Si_8B_{14}$	55
$(Co_{0.5}Fe_{0.5})_{74}Si_8B_{14}Nb_4$	85
$(Co_{0.5}Fe_{0.5})_{72}Si_8B_{14}Nb_4Cr_2$	121
$(Co_{0.5}Fe_{0.5})_{74}Si_8B_{14}Cr_4$	135



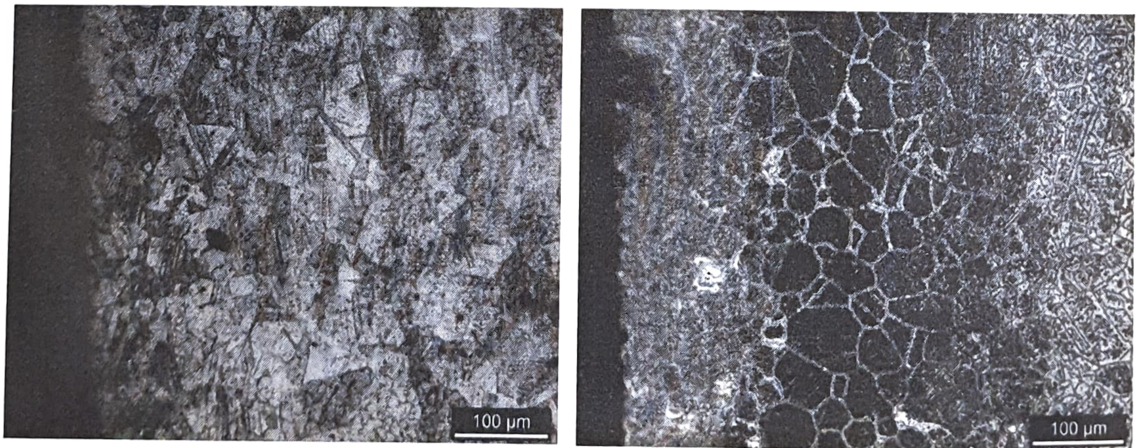
(a)



(b)

Fig. 3. (a) Giant magneto-impedance sensor and (b) sensor output for different carburized samples along with hardness data.

The optical micrographs of as-received and carburized sample (Carb-1) are shown in Fig-4a and 4b respectively. The as-received sample with granular morphology converted to one with carbide precipitation in the grain boundaries. With depletion of chromium to form carbides, there is enhancement in ferromagnetic components in the matrix leading to rise in magnetic signal. The developed GMI based sensing device can be used for detection of carburization in reactor units of petrochemical industries.



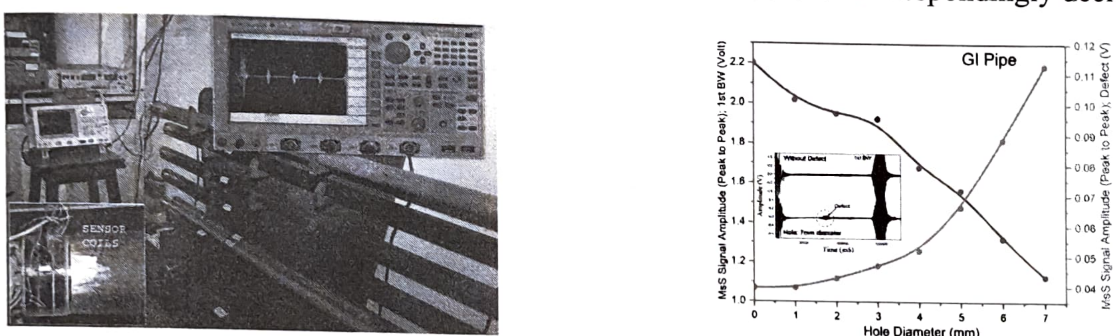
(a) (b)

Fig.4. Optical micrograph of (a) as-received and (b) Carb-1 sample.

RAPIDLY QUENCHED MAGNETOSTRICTIVE AND HIGH INDUCTION ALLOYS

Magnetostrictive materials for sensor application

In the laboratory, amorphous FeSiB based alloy ribbon having magnetostriction in the range of 25 to 30 ppm, have been used for generation of ultrasonic guided waves for detection of defects in pipes. The advantages of these soft magnetic ribbons are that they exhibit saturation magnetostriction constant in low magnetizing field and thereby high magnetizing field sources like either permanent magnets or bulky biasing coils can be eliminated. The melt Spun ribbons are pasted on one end of the pipe. Transmitting (T_c), Biasing (B_c) and Receiving (R_c) coils are placed over the magnetostrictive ribbons. The AC and DC current was sent through T_c and B_c coils. The laboratory based MsS measurement system is shown in Fig-5a. The MsS sensor output obtained as a variation of backwall (BW) echoes, and those obtained from hole as function of hole diameters are explained in Fig-5b. The magnetostrictive ribbon induces mechanical waves and transmitted through the pipe, while the reflected mechanical waves change permeability of stress sensitive ribbons due to Villari effect [18]. The change in permeability induces a secondary voltage picked up by R_c. It is observed that with increase in hole diameter, the MsS signal increases distinctly beyond one mm while the BWs correspondingly decreases.



(a) (b)

Fig.5. Photograph of (a) MsS sensor system and (b) variation of MsS signals from backwall (BWs) and those obtained from hole in the galvanized iron (GI) pipe.

Tailoring metastable alloy compositions for high induction

The proper alloy design is the basis for high saturation magnetization and Curie point, fundamentally governed by Slater-Pauling curve [19]. It describes that magnetization of Fe-Co alloys become maximum at a fixed compositional ratio than any other stoichiometric ratio for same elements even for any other ferromagnetic elements. Accordingly, the crystalline alloys with nominal composition of $Fe_{65\text{-}70}Co_{35\text{-}30}$ have been reported a maximum values of M_s (2.4 T) and T_c (1000°C)[20]. These magnetic parameters of similar type Fe-Co basic composition are deviated in amorphous alloys owing to the addition of necessary metalloids. However, the controlled annealing treatment for same amorphous alloy results in the nanocomposites with a distribution of nanocrystallites in amorphous precursor, and the M_s values of annealed alloys are superior than pre-annealed amorphous alloys. On the view point of alloy design, the amorphous and nanostructutred soft magnetic alloy consist of four different categories elements, e.g., ferromagnetic, metalloid, grain growth inhibitors and nucleating agents with different compositional ratio to achieve necessary magnetic properties. The elemental percentage affects material properties, discussed here for the alloys of nominal compositions $(Fe_{1-b}Co_b)\,100_{-w-x-y-z}B_wSi_xNb_yCu_z$ (where $0.05 \leq b \leq 0.5$ at%, $8 \leq w \leq 13$ at%, $0 \leq x \leq 8$ at%, $0 \leq y \leq 3$ at%, $0 \leq z \leq 1$ at %). Fig.6 explains the effect of ferromagnetic (Fe/(Fe+Co)) and non-magnetic (B/Nb(B+Si)) elements on saturation magnetization and coercivity. The saturation magnetization (M_s) becomes greater than 1.6 T while Fe/ (Fe+Co) and B/Nb(B+Si) vary within 0.5-0.65 and 0.3 -0.5, respectively (Figs. 6a and 6b). It is also noteworthy that the similar low range (0.5-0.65) of Fe/ (Fe+Co) ratio is also responsible for maintaining coercivity below 250 mOe (Fig. 6c). Similarly, the B/Nb(B+Si) ratio with lower range (0.15 -0.27) also leads to alloys with coercivity below 250 mOe (Fig. 6d).

Therefore, the amorphous and nanocrystalline alloys achieve high saturation magnetization and low coercivity with the optimization of alloy composition by varying ferromagnetic and non-magnetic elemental ratios.

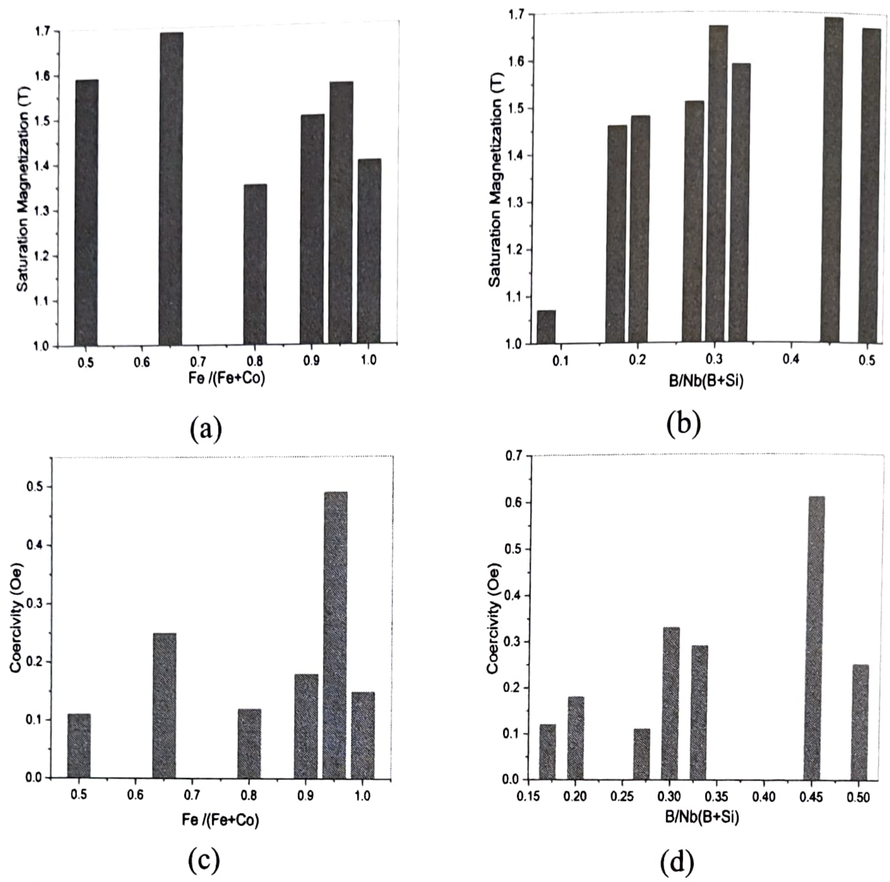


Fig. 6. Variation of saturation magnetization with the ratios of (a) Fe/(Fe+Co)), (b) B/Nb(B+Si) and coercivity with that of (c) Fe/(Fe+Co)), (d) B/Nb(B+Si)

PERSPECTIVE APPLICATION FOR EMI SHIELDING

The electromagnetic interference shielding effectiveness (EMI SE) of soft magnetic amorphous ribbons of typical composition $Co_{72.5}(SiB)_{22.5}$, $Fe_{80}(SiB)_{20}$, $Fe_{83}(SiB)_{15}Nb_2$ and $(FeCo)_{83}(SiB)_{13}Nb_3Cu_1$ were studied in the 0-8 GHz microwave frequency range. The EMI SE mechanism of typical soft-magnetic melt-spun ribbons has been described schematically (Fig. 7). The total shielding of incoming EM waves is done through attenuation by shields through surface reflection, matrix absorption and multiple internal reflection.

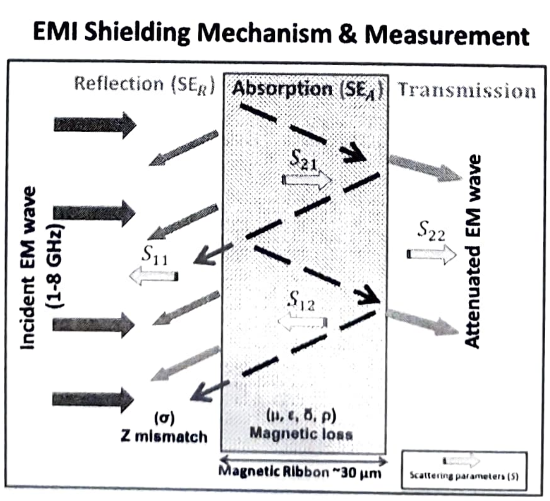


Fig. 7. Schematic representation of EMI shielding mechanism in amorphous soft magnetic ribbons.

The material parameters like complex permittivity (ε', ε"), complex permeability (μ', μ") and scattering parameters (S_{11}, S_{12}, S_{22}, S_{21}) obtained from VNA were used to calculate the reflection(SER) and absorption(SE_A) contribution from the total shielding effectiveness(SE_T) using equations 1-4 [21].

EMI $SE_T(dB) = SE_R + SE_A + SE_M$ (1) (SE_M neglected for SE_T>10dB)

$$SE_T = SE_R + SE_A \tag{2}$$

$$SE_R = 10\log_{10}\left(\frac{1}{1-|S_{11}|^2}\right) \tag{3}$$

$$SE_A = 10\log_{10}\left(1-\frac{|S_{11}|^2}{|S_{12}|^2}\right) \tag{4}$$

The complex parameters (ε', ε", μ', μ") spectrum, decreases from 0-5 GHz and remains constant till 8 GHz for all alloy ribbons. Further, the real part of complex permittivity (ε') and permeability (μ') representing energy storage part does not show difference based on alloy composition. Whereas, the imaginary or lossy part (ε", μ") show significant variation among the ribbons based on alloy composition, decreasing in the order of CoSiB, FeSiB, FeCoSiBNbCu and FeSiBNb. The total EMI SE and material properties of amorphous ribbons are given in Table. 2.

Table. 2. Summary of electromagnetic shielding and soft magnetic properties of amorphous ribbons

S.No	Alloy	SE_T (dB)	SE_A	SE_R	H_c (A/m)	M_s (T)	μ_i
1	$Co_{72.5}(SiB)_{22.5}$	>35	33	<3	3 ± 0.5	0.7	10^{4-5}
2	$Fe_{80}(SiB)_{20}$	>30	27	<3	8 ±0.5	1.5	10^{3-4}
3	$(FeCo)_{83}(SiB)_{13}Nb_3Cu1$	>33-26.5	21-30	<5	18 ±1	1.6	10^3
4	$Fe_{83}(SiB)_{15}Nb_2$	32 -12	10-20	<8	24 ±1.5	1.45	10^2

The as-quenched amorphous ribbons irrespective of composition, show good EMI shielding properties (> 10 dB) in the entire 0-8 GHz microwave frequency range. Particularly, CoSiB and FeSiB alloys show exceptional total shielding characteristics (SET >30 dB) in the entire frequency range, attenuating 99.99% of incident EM waves. Interestingly, the absorption is a main shielding mechanism in magnetic ribbons. The reflection (SE_R) contribution lies less than 5 dB, signifying, the entire EM waves enters into ribbon matrix and undergoes attenuation through absorption mechanism (SE_A). Further, the compositional dependent variation among the ribbons can be observed (Table.2). The variation is mainly attributed to the effective skin depth, in turn depends on the magnetic permeability and electrical resistivity of the alloy ribbons [22]. The present study substantiates the excellent shielding properties of soft magnetic ribbons, particularly as magnetic absorbers in 0-8 GHz frequency range. The soft magnetic ribbons can be effectively pulverized and used as magnetic filler agents in composites for broadband shields/absorbers.

CONCLUSION

The rapidly quenched materials in the form of amorphous / nanostructured wires and foils were prepared by in-water quenching and melt spinning techniques. The CoFe-based microwires reveal excellent giant magneto-impedance properties and were used as core element of a GMI based sensing device for detection of carburization in austenitic steel. The magnetostrictive sensing (MsS) device was developed with amorphous magnetostrictive ribbons as sensing element for detection of defects in pipes. The dimension change of pipe defect (e.g., hole) displayed corresponding evidence in MsS signals. Other than sensor applications, the properties of rapidly quenched ribbons where also tailored for achieving high saturation induction. For this, compositional control was carried out on metalloids (Si, B), refractory element like Nb and ferromagnetic constituents (Fe,Co) to achieve saturation induction greater than 1.6 Tesla. The rapidly quenched amorphous ribbons also manifested potential electromagnetic shielding properties. Amongst different alloy ribbons, the CoSiB and FeSiB based ribbons showed exceptional total shielding characteristics with SE_T >30 dB.

REFERENCES

[1]. Y. Yoshizawa, S. Oguma, K. Yamauchi : New Fe-based soft magnetic alloys composed of ultrafine grain structure. J. Appl. Phys 64: 6044, 1988.

[2]. Nicholas de Christofaro : Amorphous Metals in Electric-Power distribution applications.MRS Bulletin 23: 50-56, 1998.

[3]. AO. Olofinjana, J.H. Kern, H.A. Davies : Effects of process variables on the multi-strand casting of high strength sub-millimeter metallic glass wire. J. Mater. Process. Technol 155–156:1344, 2004.

[4]. P. Sarkar, R. K. Roy, A. K. Panda, A. Mitra : Optimization of process parameters for developing FeCoSiB amorphous microwires through in-rotating-water quenching technique. App. Phys A: Mater. Sc. and Proces 111: 575-580, 2013.

[5]. V.R.V. Ramanan : Metallic Glasses in Distribution Transformer Applications: An Update. J. Mater. Eng 13: 119-127, 1991.

[6]. K. Souma, S. Tanigawa, I. Moue, H. Kikuchi, T. Iwasaki : High-performance Materials for Electric Drive Solutions. Hitachi Review 60: 54-62, 2011.

[7]. M.E. McHenry, M.A. Willard, D.E. Laughlin : Amorphous and nanocrystalline materials for applications as soft magnets. Prog. Mater. Sci 44: 291, 1999.

[8]. R.K. Roy, A. K. Panda, A. Mitra : Effect of Co content on structure and magnetic behaviors of high induction Fe-based amorphous alloys. J. Magn. Mag. Mater 418: 236–241, 2016.

[9]. R.K. Roy, S. J. Kernion, S. Shen, and M. E. McHenry : Crystallization behavior and high temperature magnetic phase transitions of Nb-substituted FeCoSiBCu nanocomposites. Applied Physics Letters 99: 192506, 2011.

[10]. H. Kwun and K.A. Bartels : Magnetostrictive sensor technology and its applications Ultrasonics 36: 171–8: 1998.

[11]. A.K. Panda, P K Sharan, R. K. Roy, G.V.S. Murthy, A. Mitra : Generation and detection of guided waves in a defective pipe using rapidly quenched magnetostrictive ribbons.Smart Materials and Structures 21: 045015, 2012.

[12]. V. Zhukova, M. Ipatov, A. Zhukov : Thin magnetically soft wires for magnetic microsensors. Sensors 9: 9216–9240, 2009.

[13]. P. Ripka : Review of fluxgate sensors. Sensors & Actuators A 33: 129-141, 1992.

[14]. A.K.Panda, A.P. James, A. Mohan, S. Dey, R.K.Roy, A.Mitra : Investigation on transverse defect and cavitation depth in ferrous pipe using melt spun FeSiB ribbon as magnetostrictive sensing element. NDT&E International 80: 15-22, 2016.

[15]. T.K. Das, A. Mitra, S.K. Mandal, R.K. Roy, P. Banerji, A.K. Panda : Parametric controls on giant magnetoimpedance (GMI) behaviour of CoFeSiBCr amorphous wires for prospective sensor applications. Sens. & Actuators A 220: 382-387, 2014.

[16] V.M. Petrov, V.V. Gagulin : Microwave absorbing materials. Inorg. Mater 37:93-98, 2001.

[17]. M. Vazquez : Giant magneto-impedance in soft magnetic wires. J. Magn. Magn.Mater. 226–230: 693-699, 2001.

[18]. E. Villari : Change of magnetization by tension and by electric current Annal. Phys. Chem., Lpz. 128:1865.

[19]. J.C. Slater : The Ferromagnetism of Nickel. II. Temperature Effects. Phys. Rev. 49: 931, 1936.

[20]. F. Pfeifer, C.J. Radelo : Soft magnetic Ni-Fe and Co-Fe alloys - some physical and metallurgical aspects. J. Magn. Magn. Mater 19:190, 1980.

[21]. R. Panigrahi, S.K. Srivastava, J. Pionteck : Fabrication of elastomer blends involving core (Polystyrene)@shell (Polyaniline) approach, their characterization and applications in electromagnetic shielding. Rubber Chem. Technol 91: 97–119, 2018.

[22]. P. Murugaiyan, A. Mitra, A.K. Panda, A.S. Kumar, R.K. Roy, S. Kumar : Electromagnetic interference shielding effectiveness of soft magnetic amorphous. Physica B: Condensed Matter 568: 13-17, 2019.