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Corrosion of amorphous and nanocrystalline Fe-based alloys and its influence on their magnetic behavior

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Abstract

Nanocrystalline soft magnetic materials with low coercivity, high saturation magnetization and high permeability are commonly used as cores in transformers and generators in stress and field sensors. The influence of factors connected with corrosion is almost impossible to eliminate. In the present work, a comparative study of the electrochemical behavior of $Fe_{78}Si_{13}B_9$ and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ amorphous and nanocrystallized alloys, tested in 0.5 M NaCl solution, has been performed by linear polarization and electrochemical impedance spectroscopy methods. Changes of magnetic properties including coercivity, induction and magnetic retentivity were analyzed. These properties were investigated as a function of the structure of primary amorphous ribbons and as a function of corrosion environment type, in which longitudinally and transversely cut ribbon specimens were exposed for 15 days. The best magnetic properties were found for the $Fe_{78}Si_9B_{13}$ ribbon after a structural relaxation at a temperature of 350 °C for an hour and for the $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ ribbon after a primary crystallization at a temperature of 550 °C for an hour. Corrosion did not cause the direct degradation of the magnetic properties of the $Fe_{78}Si_9B_{13}$ and $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ alloys. The corrosion processes occurring on the surface of the $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ alloy ribbon with the amorphous structures improve induction B_s. Most probably it is connected with the decrease of undesirable stresses blocking a motion of magnetic domain walls on the ribbon surface. Changes of corrosion mechanism depending on structure and applied solution were analyzed. The electrochemical impedance experiment were performed at open circuit potential for amorphous and nanocrystalline specimens. Two electrochemical corrosion mechanisms of $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ alloy in 0.5 M NaCl solution were found. Charge transfer control mechanism is typical for amorphous (as received) alloys. Mixed mechanism-mass transport and charge transfer controlled was observed for nanocrystalline $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ alloy.

Keywords: Soft magnetic materials; Amorphous structure; Nanocrystalline structure; Electrochemical impedance spectroscopy; Fe-based alloy

1. Introduction

Nanocrystalline ferromagnetic iron based alloys are among the most interesting in the area of magnetic materials engineering. Due to their special structure and corresponding novel properties, the interest in these alloys has increased rapidly. These are two types of new generation soft magnetic Fe-based materials: single-phases (amorphous structure), i.e. Metglas and two-phases nanocrystalline structure, i.e. Finemet or Nanoperm. Presently there is not any norm of classification this group of materials. But this alloys can be described in general as [1–5]:

$$TL_{1-x}(TE, M, NM)_x \quad (1)$$

where TL is the ferromagnetic transition metal element: Fe; Co; Ni, TE the transition metal element: Zr; Nb; Hf; Ta, M and metalloid: B; C; P; Si and NM is a noble metal: Cu, Ag, Au.

Nanocrystalline soft magnetic materials with low coercivity, high saturation magnetisation and high permeability are commonly used as cores in transformers and generators, stress and field sensors in a technological application. Due to their numerous application nanocrystalline iron based alloys often work in a wet industrial and marine atmosphere containing sulphide and chloride ions.

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When corrosion creates the need for system replacement, costs can run in the millions of euro. Corrosion can result in sudden, hazardous leaks with potentially catastrophic consequences—especially when combustible fluids, very high temperatures or pressure vessels are involved. That is why the risk of various corrosion process needs to be considered [6–13]. It is impossible eliminate the interaction between magnetic materials and environment. It leads to an electrochemical corrosion. Corrosion can change structure and properties of Fe-based alloys In general the corrosion resistance of most amorphous metallic materials is determined by the composition, stability, and uniformity of the composition and stability and uniformity of the surface film formed as well as the kinetic of formation passive film. The physical properties, such a corrosion resistance, in amorphous metallic materials mostly depends on their structure and phase compositions [10,12–14]. The corrosion products formed on the surface of a ferromagnetic alloy may cause a partial degradation of soft magnetic properties.

2. Experimental procedure

Amorphous alloys of chemical composition in atomic concentration (Fe: 73.5%, Si: 13.5%, B: 9%, Nb: 3%, Cu: 1%) and (Fe: 78%, Si: 13%, B: 9%) were obtained by planar-flow casting technique. Information concerning structure, annealing parameters are shown in Table 1. The structure of amorphous and nanocrystalline specimens were analyzed by X-ray diffraction using Co Kα radiation. The grain size of α-Fe(Si) crystallites was calculated from X-ray diffraction spectra peak using the Scherrer Eq. (2) based on the survey of diffraction line width:

$$d = \frac{0.9\lambda}{B\cos\theta_B} \quad (2)$$

where d is the crystalline particle diameter (nm), B the widening of diffraction line measured in the middle its maximum intensity (radian), λ the length of X-radiation wave (nm) and θ_B is the diffraction angle of beam of radiation corresponding with Bragg's maximum (°).

The electrochemical behavior and corrosion process were studied in chloride solution. A 0.5 M solution of NaCl was prepared from analytical grade reagents and deionized and dematerialized water. The solution have been deoxygenated prior to every electrochemical measurement. The ribbons of both alloys (working electrodes) before each measurement were cleaned in acetone and next covered of the protective layer exception of tested part of surface having about 1 cm^2 area in each ribbons. The corrosion tests were performed on the shiny side, which were not in contact with the cooling wheel in process of casting.

The electrochemical behavior of investigated alloys have been performed by linear polarization and electrochemical impedance spectroscopy technique (EIS) in third electrode cell. The auxiliary electrode was a platinum foil and the saturated calomel electrode (SCE) as a reference. Tests were conducted using an Eco Chemie B.V PGSTAT30 Potentiostat and accompanying software GPES (General Purpose Electrochemical System) and FRA (Frequency Response Analyzer System).

The polarization curve and impedance data were obtained after holding the samples at open circuit potential for 20 min. In the anodic polarization tests, the alloy was scanned at the rate 4 mV/s from negative (cathodic) overpotential and ending at positive (anodic) overpotential. The scan rate was chosen to be slightly high to avoid total anodic dissolution of the very thin samples prior to the completion of the test. The EIS measurements were made in the frequency range between 20 kHz and 1 Hz.

Coercivity Hc and saturation magnetization Bs were measured at room temperature for 2 mm × 3 mm × 0.024 mm ingots in amorphous, amorphous relaxed and nanocrystalline states in a Lake Shore Crytronics Inc. Vibrating Sample Magnetometer. The magnetic behavior evaluation of the samples exposed to 0.5 M NaCl solution for 15 days was carried out by using saturation magnetization Bs and coercivity Hc. The cross-sectional area was recalculated after each ribbon corrosion exposure.

Table 1
Corrosion and magnetic properties of $Fe_{78}Si_9B_{13}$ and $Fe_{73.5}Si_{13.5}B_9Nb3Cu_1$ alloy tested in 0.5 M solution of NaCl

	Structure		
	Amorphous	Amorphous relaxed at 350 °C	Nanocrystalline
$Fe_{78}Si_9B_{13}$			
Corrosion parameters			
E_{corr}, mV	−735	−903	−765
v_{corr}, mm/year	0.9	0.36	0.13
Magnetic parameters			
Hc, $A/m_{noncorroded}$	12.6	11.14	
Hc, $A/m_{corroded}$	13.6	36.83	
Bs, $T_{noncorroded}$	1.84	2.39	
Bs, $T_{corroded}$	1.72	1.98	
$Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$			
Corrosion parameters			
E_{corr}, mV	−605	−430	−515
v_{corr}, mm/year	0.12	0.8	0.31
Magnetic parameters			
Hc, $A/m_{noncorroded}$	7.67		0.57
Hc, $A/m_{corroded}$	4.09		3.82
Bs, $T_{noncorroded}$	0.84		0.8
Bs, $T_{corroded}$	0.88		0.66

3. Results and interpretation

Investigated alloys represent two groups of modern Fe-based soft magnetic materials. The alloys in the initial state had single-phase amorphous structure achieved as a result of cast. The $Fe_{78}Si_9B_{13}$ alloy has characterized single-phase amorphous structure after heat treatment at the temperature of 350 °C (structural relaxation) and has achieved the best soft magnetic properties. The $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ alloy had the best soft magnetic properties when its structure have been diphase: