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## Electrochemical corrosion and its influence on magnetic properties of $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$ alloy

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**Abstract:** 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. The influence of factors connected with a corrosion is almost impossible to eliminate. From this reason the investigations in the direction of knowledge of an electrochemical corrosion mechanism and its influence on magnetic properties of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$  alloy were performed. In the present work, a comparative study of the electrochemical behaviour of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$  amorphous, amorphous relaxed and nanocrystallized alloy tested in 0.5 M  $\text{Na}_2\text{SO}_4$  solution, has been performed by means of electrochemical technique: direct – current technique (anodic polarization). Regardless of structure, the multicomponent alloy  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$  had an ability to passivation in the sulphate solution. Changes of magnetic properties including coercivity, magnetization were analyzed. These properties were investigated as a function of the produced structure in primary amorphous ribbon and exposure specimens for 15 days in corrosive environment.

**Keywords:** Fe-based materials, Amorphous structure, Nanocrystalline structure, Electrochemical properties, Magnetic properties,

### 1. INTRODUCTION

Nanocrystalline ferromagnetic iron based alloys are among the most interesting materials in the area of magnetic materials engineering. Due to their special structure and corresponding novel properties, the interest in these alloys has increased rapidly during the past 15 years. Nanocrystalline soft magnetic materials with low coercivity, high saturation magnetisation and high permeability are commonly used as the cores in transformers and generators, a 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. It is impossible eliminate the interaction between magnetic materials and environment. It leads to an electrochemical corrosion. The corrosion can changes 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. The high temperature is an additional factor accelerating the corrosion rate. The corrosion products formed on the surface of a ferromagnetic alloy may cause a partially degradation of soft magnetic properties [1 – 8].

The DC current (Potentiodynamic polarization) were used to analyse the corrosion resistance in sulphide solution at temperature of 20°C. In recent years the structural relaxation and crystallization provided information of diffusion process, which influence magnetic properties (i.e. coercivity, magnetization, retentivity etc) and corrosion resistance. Another point little investigated of amorphous and nanocrystalline Fe – based alloys, obtained by planar – flow casting process is the influence of the structure and corrosion on the magnetic properties of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$  alloy. The ribbon surface in contact with the wheel during the quenching procedure is cooled at the maximum speed, except the case of local defects due to impurities, roughness and gas bubbles present on the wheel itself. This surface appears dull and is generally known as the ‘dull side’. On the surface not in contact with the wheel undergoes a more regular cooling, so this side is able to retain the shape of the liquid layer from which it comes, and this side is called ‘shiny side’[10].

The commercial  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$  nanocrystalline alloy are produced by planar – flow casting process and latter heat treated mainly used as transformer core owing to their excellent soft magnetic properties. The magnetic properties, crystallization kinetics and structural changes of the alloy have been studied extensively, but the electrochemical properties and influence of the corrosion on the magnetic properties of these alloys are still not recognized well [11, 12].

Such studies are essential for the widespread commercial utilization for these alloys under normal atmospheric treatment. The goal of this paper was to study the effect of structural changes such as structural relaxation and crystallization on magnetic properties and corrosion resistance of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$  alloy, also study the electrochemical behavior and mechanism of the corrosion of amorphous, amorphous relaxed and nanocrystalline  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_3\text{Cu}_1$  alloy in 0.5 M  $\text{Na}_2\text{SO}_4$  solution.

## 2. EXPERIMENTAL PROCEDURE

Amorphous alloy of chemical composition in atomic concentration (Fe – 73,5%, Si – 13,5%, B – 9%, Nb – 3%, Cu – 1%) was obtained by planar – flow casting technique. Information concern structure, annealing parameters and geometrical characterizations are shown in table 1. The structure of the amorphous and nanocrystalline specimens were analyzed by X-ray diffraction using  $\text{Co-K}\alpha$  radiation. The grain size of  $\alpha\text{Fe}(\text{Si})$  crystallites was calculated from X-ray diffraction spectra peak using the Scherrer equation (1) based on the survey of diffraction line width [13]

The electrochemical behavior and corrosion process was studied in sulphate solution. A 0.5 molar solution of  $\text{Na}_2\text{SO}_4$  was prepared from analytical grade reagents and deionized and dematerialized water. The ribbons were cleaned in acetone and next covered of the protective layer exception of tested part of surface having about  $0.5\text{ cm}^2$  area in each ribbons. The corrosion test were performed on the shiny side of the sample, which were not in contact with the cooling wheel in process of casting. This side of the sample was used as a working electrode

The electrochemical behavior of investigated alloy were performed basing on polarization curves registration using anodic polarization technique (AP) The auxiliary electrode was a platinum foil and  $\text{Hg}/\text{HgSO}_4$  electrode as a reference. AP tests were conducted using an Eco

Chemie B.V PGSTAT30 Potentiostat and their using their accompanying software GPES (General Purpose Electrochemical System).

The polarization curve were obtained after holding the samples at open circuit potential for 20 minutes. In the anodic polarization tests, the alloy was scanned at the rate 4 mV/sec. from negative (cathodic) overpotential and ending at positive (anodic) overpotential. The scan rate was chosen to be slightly high so as to avoid total anodic dissolution of the very thin samples prior to the completion of the test.

The passivation ability and corrosion resistance of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy have been determined basing on the measurement of the following values: corrosion potential  $E_{\text{corr}}$  [mV], corrosion current density  $i_{\text{corr}}$  [ $\text{A}/\text{cm}^2$ ], GPES program using I<sup>st</sup> Stern – Tafel method, enabled to set corrosion rate express by  $v_{\text{corr}}$  [mm/year]. The surface area (SA), equivalent weight (EW) and the density (D) of electrode material are used to calculate the corrosion rate in terms of current density ( $I_{\text{corr}}$ ) and millimeters/year ( $v_{\text{corr}}$ ), equation 2 and 3 [14].

$$I_{\text{corr}} = i_{\text{corr}} / SA, \text{ A}/\text{cm}^2 \quad (2)$$

$$v_{\text{corr}} = 3272 \cdot i_{\text{corr}} \cdot \text{EW}/(\text{SA} \cdot \text{D}) \quad (3)$$

Coercivity  $H_c$  and saturation magnetization  $B_s$  were measured at the room temperature for  $2 \times 3 \times 0.024$  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  $\text{Na}_2\text{SO}_4$  solution for 15 days was carried out by using the saturation magnetization  $B_s$  and coercivity  $H_c$ . The cross sectional area was recalculated after each ribbon corrosion exposure.

### 3. RESULTS AND DISCUSSION

For selected samples the structural changes were observed by applying X-ray method. The quenched and samples annealed at temperature of  $450^\circ\text{C}$  were amorphous. Sample annealed at temperature of  $550^\circ\text{C}$  for 1 hour, structure of this sample consist of amorphous matrix and nanocrystalline grains  $\alpha\text{Fe}(\text{Si})$  phase (about 20 nm) embedded in amorphous matrix. Information concern annealing parameters and structure shown in table 1.

The different electrochemical behavior of amorphous alloy can be explained in terms of their structure. The alloy was subjected to anodic polarization in the as received state as well as after devitrification. In this way, it was possible to compare the difference in electrochemical response dependent on structure of the alloy. The anodic polarization curves of amorphous and selected annealed ribbons obtained in 0.5 M  $\text{Na}_2\text{SO}_4$  solution are given in Figure 1. It was observed active – passive region in the shape of potentiodynamic curve corresponding to  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  as quenched and nanocrystalline ribbons in 0.5 M  $\text{Na}_2\text{SO}_4$  solution at  $20^\circ\text{C}$ . It was observed two maximum (Figure 3). The first maximum appears at potential  $E_1 = -0.07$  mV and correspond to current density  $I_1 = 0.002$   $\text{A}/\text{cm}^2$ , and the second maximum appears at potential  $E_2 = +0.60$  V and correspond to current density  $I_2 = 0.006$   $\text{A}/\text{cm}^2$ . A significant dissolution of the most chemically active alloy's element was stopped only after formation of  $\text{FeOOH}$  film. The first maximum on potentiodynamic curve (C on Figure 1) was corresponded to formation  $\text{FeOOH}$  adsorbed film. The increasing of the potential provokes destruction of  $\text{FeOOH}$  film and form stable passive  $\gamma$  –  $\text{Fe}_2\text{O}_3$  and probably  $\text{SiO}_2$  film on the ribbon. Probably the second maximum is responsible

for building passive film [15]. The amorphous relaxed ribbons did not exhibit active – passive transition or passivation. These samples were destroyed during anodic polarization.

The value of corrosion potential  $E_{\text{corr}}$  and corrosion rate  $v_{\text{corr}}$  of amorphous and heat treated  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy ribbons tested in 0.5 M  $\text{Na}_2\text{SO}_4$  at 20°C obtained from potentiodynamic polarization curves and the 1<sup>st</sup> Stern – Tafel method are summarized in Table 1. The dependence between temperature of the heat treatment and corrosion rate  $v_{\text{corr}}$  of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy obtained in 0.5 M  $\text{Na}_2\text{SO}_4$  solution shows Figure 2.

Tafel extrapolation can be complicated by several factors. There are resistivity of the solution, cell geometry, location of the reference electrode and magnitude of applied current. This technique is precision enough for estimate, which state of the alloy – amorphous, amorphous relaxed or nanocrystalline, have better corrosion resistance.

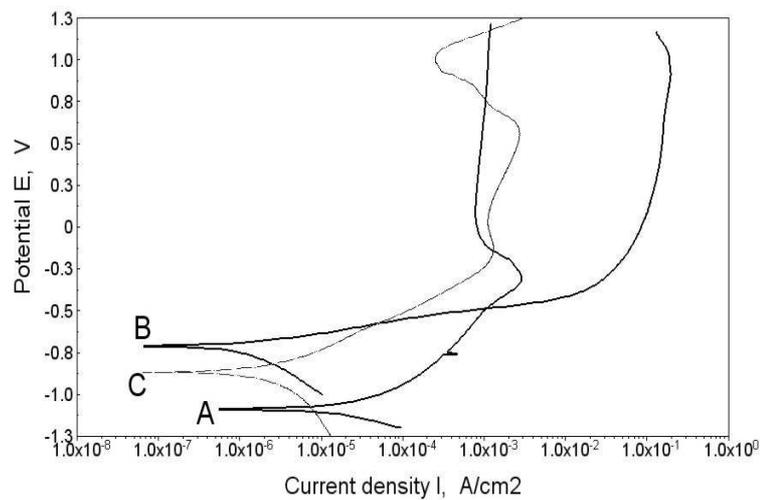


Figure 1. Potentiodynamic polarization curves corresponding to the as quenched (A), heat treated at 450°C (B), and heat treated at 550°C (C)  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy in 0.5M  $\text{Na}_2\text{SO}_4$  solution.

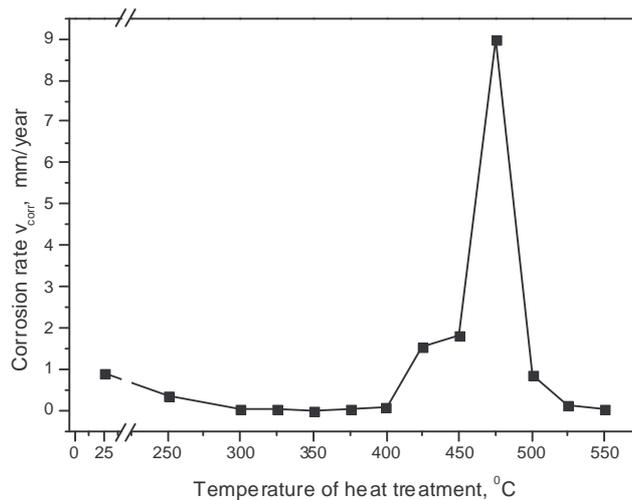


Figure 2. The dependence between temperature of the heat treatment and corrosion rate of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy obtained in 0.5 M  $\text{Na}_2\text{SO}_4$

Heat treatment leading to structural relaxation of amorphous phase favour improvement of the corrosion resistance of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy. The corrosion rate of amorphous relaxed ribbons is smaller than the amorphous as received one.

Crystallization of the  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy that leads to nanocrystalline alloy formation, increases the corrosion resistance. Corrosion rate of the nanocrystalline ribbon was smaller than the amorphous ribbon. Generally the structural relaxation have improved corrosion resistance in 0,5 M  $\text{Na}_2\text{SO}_4$  solution. But the heat treatment at temperature range from 425°C to 475°C caused considerable increasing of the corrosion rate.

Probably before nanocrystallization beginning of the amorphous  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy, Cu cluster were formed and then amorphous phase changed the chemical composition from place to place [16]. A differences in a value of electrochemical potential between regions in amorphous matrix is significant and it provokes intensive electrochemical corrosion. It was the reason why the corrosion rate was so high for alloy before first step of nanocrystallization.

The magnetic properties of Fe-based amorphous and nanocrystalline alloy are strongly affected by the surface quality of melt spun ribbons. We showed that the reduction in an incidence of surface features such a roughness, leads to the decrease in the coercive and increase in the magnetization of this alloy. Defects act as pinning sites which impede domain wall motion [17]. As a thickness (around 24µm) of the ribbon was small, the surface phenomena are important to Bs and Hc, therefore the influence of the surface phenomena must be taken into consideration.

Table 1.

Heat treatment parameter, structure, corrosion and magnetic properties of  $\text{Fe}_{73,5}\text{Si}_{13,5}\text{B}_9\text{Nb}_9\text{Cu}_1$  alloy tested in 0,5 M solution of  $\text{Na}_2\text{SO}_4$  for 15 days.

Heat treatment parameters		Structure	Corrosion parameters		Magnetic parameters							
			$E_{\text{corr}}$ , mV	$v_{\text{corr}}$ , mm/year	Hc, A/m		Bs, T					
Temperature, °C	Time, h				noncorroded	corroded	noncorroded	corroded				
As quenched	—	Amorphous	-1095	0.927	7.67	4.09	0.84	0.88				
250	1	Amorphous relaxed	-1168	0.390	6.08	12.30	0.74	0.82				
300			-710	0.051	—	—	—	—				
325			-800	0.034								
350			-769	0.001								
375			-913	0.041								
400			-809	0.117								
425			-762	1.577								
450			-692	1.837					2.38	6.49	0.69	0.86
475			-1001	9.00					—	—	—	—
500			-689	0.859	0.95	3.82	0.84	0.66				
525		-868	0.150	—	—	—	—					
550		-843	0.055	0.57	3.82	0.80	0.66					
			Nanocrystalline: amorphous + $\alpha\text{Fe}(\text{Si})$									

#### 4. CONCLUSIONS

- The magnetic properties of Fe-based amorphous and nanocrystalline alloy are strongly affected by the surface quality of melt spun ribbons. The reduction an incidence on the surface such as local defects caused by the impurities, roughness and gas bubbles, improves the magnetic properties: decrease the coercive  $H_c$  and increase in the magnetization  $B_s$  of  $Fe_{73,5}Si_{13,5}B_9Nb_9Cu_1$  alloy. As a thickness of the melt spun ribbon of the soft magnetic Fe-based alloys was small, the surface phenomena are important to magnetic properties, therefore the influence of the surface phenomena must be considered.
- The best magnetic properties of  $Fe_{73,5}Si_{13,5}B_9Nb_9Cu_1$  alloy was achived by the heat treatment that caused primary cristallization of the amourphous phase. During the annealing at temperature of  $550^\circ C$  amorphous alloy were transformed from amorphous structure to a mixed structure of  $\alpha Fe(Si)$  and amorphous matrix. The decrease of saturation magnetization was observed in nanocrystalline sample exposed for 15 days in corrosive enviroment (0.5 M  $Na_2SO_4$  solution at temperature of  $20^\circ C$ ). The soft magnetic properties of nanocrystalline  $Fe_{73,5}Si_{13,5}B_9Nb_9Cu_1$  alloy, which are seen as a relevant, can be lost while the progress in corrosion.

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