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Corrosion resistance of amorphous $Fe_{78}Si_{13}B_9$ alloy

D. Szewieczek, A. Baron

Institute of Engineering Materials and Biomaterials, Silesian University of Technology
Konarskiego 18a St., 44-100 Gliwice, Poland

In the present work, a comparative study of the corrosion behaviour of $Fe_{78}Si_{13}B_9$ amorphous, amorphous relaxed and nanocrystallized alloy tested in 0,5 M H_2SO_4 solution, has been performed by means of electrochemical technique. The influence of the quallity surface and structure on the electrochemical behaviour of $Fe_{78}Si_{13}B_9$ alloy in three states was examined.

1. INTRODUCTION

Amorphous and naocrystalline metallic materials Fe – based have attracted attention due to fact, that they have interesting properties.These alloys shows a good combination of low coercive force, low core loss and high permeabillity. These properties indicate that amorphous and naocrystalline metallic materials Fe – based, may have applications in several kinds of magnetic parts and devices, such as power transformers, data comunication interface components, electro – magnetic interference prevention components, magnetic heads, sensors, magnetic shielding and reactors[1, 2].

It is important to consider the affect, because normal atmospheric corrosion and pitting corrosion are unvoidable in many applications where soft – magnetic alloys are used and the S and Cl ions are presented, specialy at industrial and marines enviroments. 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 [3, 4, 5, 6, 7]. Amorphous metallic materials Fe – based obtained by rapid soldification of the liquide are metastabile and strives after equilibrium by structural relaxation and crystallization at temperature T_x [10]. The structural relaxation of amorphous metallic alloys are strongly infuenced by diffusion in amorphous state, and undergo changes below cristallization temperature.

The structural relaxation and crystallization provided information of diffusion process, which influence phisical properties and corrosion resistance too. Another point little investigated of amorphous Fe – based alloys, obtained by planar – flow casting process is the possible diffrent corrosion behaviour of the two sides of the ribbons. 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 liqiude layer from which it comes, and this side is called 'shiny side'[8].

The Fe – Si – B comercial amorphous alloys are produced by planar – flow casting process and mainly used as transformer core owing to their excellent soft magnetic properties. The magnetic properties, crystallisation kinetics and structural changes of Fe – Si – B alloys have been studied extensively, but the electrochemical properties of these alloys are still not well known. Such studies are essential for the widespread commercial utilisation for these alloys under normal atmospheric treatment. The goal of this paper was to study the effect of structural changes such a structural relaxation and crystallisation on amorphous alloys $Fe_{78}Si_{13}B_9$ corrosion resistance.

2. EXPERIMENTAL PROCEDURE

Amorphous alloy of chemical composition in atomic concentration (Fe – 78%, Si – 13%, B – 9%) was obtained by planar – flow casting technique. Informations concer structure, anneling parameters and geometrical characterisations are shown in table 1. The roughness of two of ribon's side were analyzed using Surtronic 3+ (Taylor – Hobson) equipment and R_a parametr was investigated.

The corrosion resistance of investigated alloys, have been determined basing on polarization curves registration using potentiodynamic method. Potentiodynamic polarization curves were performed at a scan rate of 1 mV/s using a 0,5 M H_2SO_4 solution. All polarization curves were obtain at 25±1°C, using surface of the ribbon as a working electrode. The auxiliary electrode was a platinum foil, and the saturated calomel electrode was used as a reference. Polarization curves in this work were carried out in PGP 201VoltaLab[TM]21 potentiostate, and analyzed using their accompanying software „Radiometer Elektrochmistry".

Table 1
Structure and ribbon's geometry of $Fe_{78}Si_{13}B_9$ alloys

Samples	Structure	Phases	Roughness of ribbon's surface R_a ,μm		Ribbon's dimension, mm	
			$S^{(1)}$	$D^{(2)}$	thickness	width
1	Amorphous	A	0,71	1,06		
2	Amorphous relaxed at 370°C/1h	A	0,59	0,86	0,02	7,0
3	Nanocrystalline after primary cristallization at	A+αFe(Si) $d^{(3)}$= 40nm	0,81	1,02		

$^{(1)}$ Shinny side of the ribbon

$^{(2)}$ Dull side of the ribbon

$^{(3)}$ Grain size of αFe(Si) crystallities was calculated using the Scherrer equation

Specimens measuring 5 cm were cleaned with pure ethyl alcohol and next covered by the protective layer, except tested part of surface with the 1cm^2 area in each tape. The passivation ability and corrosion resistance of $Fe_{78}Si_{13}B_9$ alloy have been determined basing on the

measurement of the following values: corrosion potential E_{corr} [mV], corrosion current density i_{corr} [A/cm^2], criticall potential passivation E_{kp} [mV], criticall density passivation current i_{kp} [A/cm^2]. "Radiometer Electrochemistry" programm using Ist Stern – Tafel method, enabled to set corrosion rate express by v_{corr} [mm/year].

3. RESULTS AND DISCUSSION

Figures 1, 2 and 3 shows the potentiodynamic polarization curves both sides (dull and shiny) amorphous, amorphous relaxed and nanocrystalline ribbons, which were examineted in 0,5 M H$_2$SO$_4$ solution.
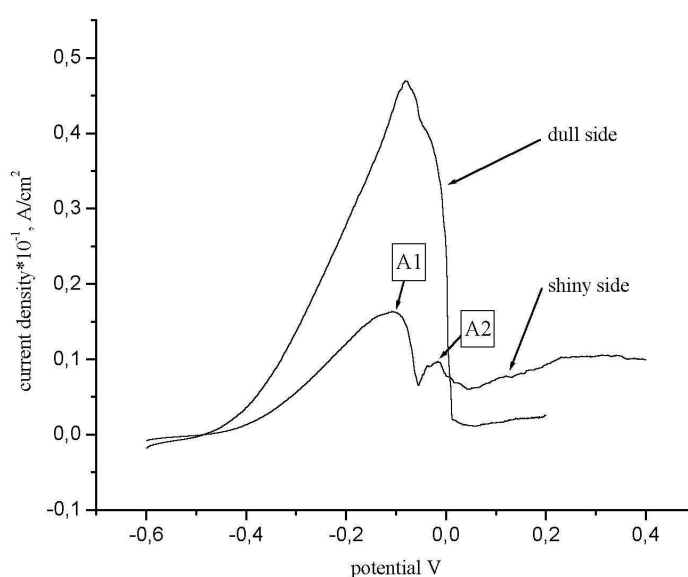

Figure 1. Potentiodynamic curves corresponding to the amorphous alloy Fe₇₈Si₁₃B₉ tested in a 0,5 M H$_2$SO$_4$ solution. A1-first point of passivation, A2-secound point of passivation

The shape of polarization curves of Fe₇₈Si₁₃B₉ alloy in three states was similar. When the potential was increasing above the corrosion potential E_{corr}, the current density increased monotonically with the electrode potential. It was noticed large differences between value of critical density current (i_{kp}) passivation the shiny and the dull side of amorphous and nanocrystalline specimens. The critical density current (i_{kp}) passivation of amorphous alloy was 16,36 mA/cm^2 for shiny side, and i_{kp} = 48,30 mA/cm^2 for dull side. For shiny side of nanocrystalline alloys i_{kp} = 210,09 mA/cm^2.
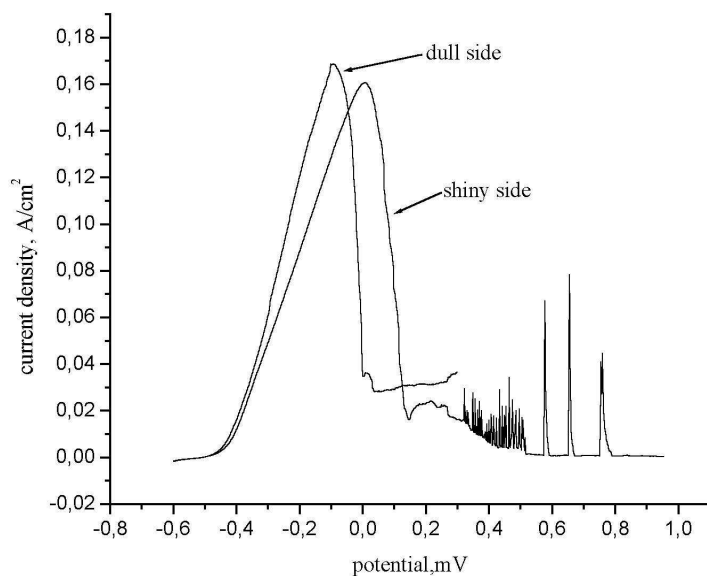
Figure 2. Potentiodynamic curves corresponding to the amorphous relaxed alloy $Fe_{78}Si_{13}B_9$ tested in a 0,5M H_2SO_4 solution
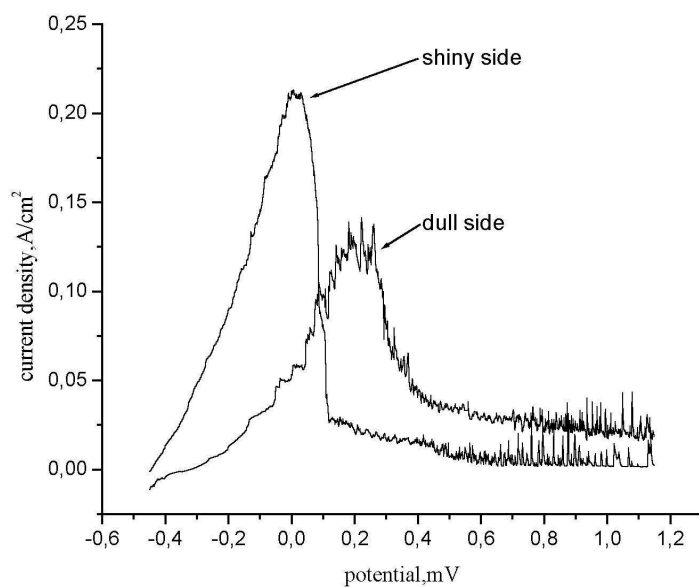

Figure 3. Potentiodynamic curves corresponding to the nanocrystalline alloy $Fe_{78}Si_{13}B_9$ tested in a 0,5 M H_2SO_4 solution

Potentiodynamic curve was very irregular for dull side of ribbon, because of strongly dissolution in nanocrystalline state. The value of the critical density current passivation $i_{kp} = 132,11$ mA/cm^2 was obtained by extrapolation. However the potentiodynamic curves of

the ribbons after structural relaxation at 370°C(1 hour) had not so large difference between critical density current passivation: the shiny side (i_{kp} = 160,70 mA/cm^2) and the dull side (i_{kp} = 168,50 mA/cm^2). These results have suggested relation between structural relaxation and corrosion resistance of amorphous $Fe_{78}Si_{13}B_9$ alloy.

The shape of potentiodynamic curve corresponding to the shiny side of $Fe_{78}Si_{13}B_9$ amorphous alloy tested in a 0,5 M H_2SO_4 solution was different to the rest of obtained curves. It was observed two points, marked as A1 and A2 (figure 1). The point A1 appears at potential E_{kp} = – 108,4 mV and correspond to current i_{kp} = 16,36 mA/cm^2, and the point A2 appears at potential E_{kp} = – 16,8 mV and correspond to current i_{kp} = 9,72 mA/cm^2. Table 2 presents electrochemical corrosion parameters obtained from potentiodynamic polarization curves and Ist Stern – Tafel method (v_{corr}).

Table 2
Electrochemical corrosion parameters of $Fe_{78}Si_{13}B_9$ alloy

sample	ribbon side	test solution[4]	E_{corr} mV	i_{corr} A/cm^2	E_{kp} mV	i_{kp} A/cm^2	v_{corr} mm/year
1	S		- 498,5	0,54	- 108,4	16,36	6,41
	D		- 515,2	0,83	- 98,2	48,30	9,76
2	S	0,5 M	- 513,4	0,29	1,8	160,70	3,47
	D		- 511,6	1,11	- 100,2	168,50	6,40
3	S		- 474,0	0,62	1,8	210,09	13,06
	D		- 478,7	0,48	28,8	132,11	5,64

[4] Amount of H_2SO_4 concentration

A significant dissolution of the most chemically active alloy's element was stopped only after formation of ferric oxide passive film. So the A1 point can be understood as oxidation of iron, according to the equation (1):

$$Fe \rightarrow Fe^{2+} + 2e \qquad (1)$$

The increasing of the potential provoke destruction of ferric oxid film and form stable passive silicon oxid film on the ribbon. Probably the A2 point is responsible for building a silicon oxide rich film [9]. The scane rate was to low to avoid total anodic dissolution of the thin samples. It is worthwhile mentioning that the 'passivation' in this text means a marked decrease in anodic activity, and not conventional passivation whereby anodic activity becomes close to zero [8].

Some authors reported the beneficial effect of primary crystallization of amorphous alloys with Si content on corrosion resistance [7, 8]. However our results indicate a degradation effect of nanocrystallization on the corrosion resistance of $Fe_{78}Si_{13}B_9$ amorphous alloy. The decrease of corrosion resistance the nanocrystalline samples can be explained by the formation of α-Fe(Si) crystalline phase, that has greater corrosion susceptibility in comparsion to the amorphous phase one [11].

4. CONCLUSIONS

It was found that corrosion resistance of $Fe_{78}Si_{13}B_9$ alloy depends on the surface's quallity and structure of this alloy. Better corrosion resistance was obserwed for the shiny side of ribons, with lower roughness, in comparsion with dull side for amorphous and nanocrystalline aloys states. The amorphous relaxed ribbon have similar electrochemical corrosion parameters for both sides. Both structural relaxation and nanocrystallization decrease the corrosion resistance of analyzed alloy.

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