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EFFECT OF COBALT AND NICKEL ALLOYING ON CORROSION BEHAVIOUR OF AMORPHOUS Fe-B-Si ALLOYS

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ABSTRACT

The electrochemical corrosion behaviour of amorphous and crystalline $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloys are studied and compared to that of the basic $Fe_{78}B_{13}Si_9$ alloy in order to evaluate the effect of alloying with both cobalt and nickel on their corrosion resistance. The amorphous alloys were obtained in the form of ribbons (thickness 25 μm) by rapid quenching from melts. The structure of the alloys was characterized by XRD, SEM, TEM and DTA techniques. The corrosion behaviour of the alloys were studied by electrochemical potential-sweep technique and gravimetric measurements, using 1N H_2SO_4, 1N NaCl and 1N NaOH as model corrosive environments.

The heat treatment of amorphous alloy samples at $700^oC/3$ h (above the crystallization temperatures of both alloys) results in crystallization of the alloys and formation of multiphase microcrystalline structures composed by α-Fe, $Fe_3(Si,B)$ as well as Co, Co_3Fe_7, $FeNi_3$, Ni_2Si_2 crystalline phases for $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloy. It is established that the corrosion rate of $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloy in all media is much lower (1-2 orders of magnitude) in comparison to $Fe_{78}B_{13}Si_9$ alloy. Thus, the additional alloying with both Co and Ni leads to considerable decrease of the rate of anodic metal dissolution reaction and increase of the susceptibility of Fe-B-Si alloy to passivation and stability of its passive state. Both alloys in amorphous state possess higher corrosion resistance than their crystalline counterparts.

Keywords: amorphous alloy, iron base, alloying, electrochemical measurements, corosion behaviour.

INTRODUCTION

The amorphous Fe-B-Si alloys possess valuable magnetic, electric and mechanical characteristics and they find already applications as soft magnetic materials in electronics, aircraft, airspace and electric industry [1-5]. An effective route for additional improvement of their magnetic and mechanical properties is alloying with cobalt, nickel or carbon [4].

It is well known that the corrosion resistance of amorphous alloys is also an important characteristic of those materials since they are employed usually as very thin plates and any corrosion damage or formation of surface film of corrosion products may change their properties unfavorably or reduce considerably their service life. The possibility to affect corrosion resistance of the amorphous Fe-B-Si alloys by heat treatment [6-9] stimulates also interest in the effect of thermally induced structural changes on electrochemical behaviour of those materials.

The literature data for the effect of alloying with Co and Ni on corrosion properties of the alloys of the system Fe-B-Si are very limited. Thus, it is shown [10-11] that alloying of Fe-B-Si alloys with cobalt results in improvement of their corrosion resistance in acidic media, the effect being more strongly expressed for the alloy in amorphous state than its crystalline counterpart. The crystallization of the amorphous $Fe_{71}Co_{10}B_{14}Si_5$ alloy upon heat-treatment however leads to increase of the rates of both cathodic hydrogen evolution and anodic metal dissolution reactions, thus reducing significantly the corrosion resistance of the alloy. In a previous paper [12] some preliminary results on corrosion behaviour of amorphous $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloy in acidic environment have been reported and it has been pointed out that the corrosion resistance of the alloy with nanocomposite structure (composed by an amorphous alloy matrix and nanosized crystals) is higher than that of the alloy with a microcrystalline structure.

The aim of the present work is to study electrochemical corrosion behaviour of amorphous and crystalline $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloys and compare to that of the basic $Fe_{78}B_{13}Si_9$ alloy in order to evaluate generally the effect of alloying with both nickel and cobalt on corrosion resistance of the alloy.

EXPERIMENTAL

The amorphous $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ and $Fe_{78}B_{13}Si_9$ alloys were obtained in the form of thin ribbons (10 mm wide and 25-30 µm thick) by rapid quenching from melt and kindly supplied by Institute of Metals Science - BAS. Two types of alloy samples were used: as-quenched and heat-treated at 700°C for 3 h - above the crystallization temperature of both alloys (645°C for $Fe_{78}B_{13}Si_9$ and 665°C for $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ respectively) in evacuated quartz tubes.

The thermal stability of the amorphous alloy was studied by Differential Thermal Analysis - DTA (Netch derivatograph, 10°/min) and the temperatures of crystallization of the alloys were determined from DTA-curves. The structure of the alloy samples was characterized by X-ray Diffraction analysis - XRD (PW 1730/10 Diffractometer) and Transmission Electron Microscopy - TEM (Philips EM-400).

The electrochemical and corrosion behaviour of the alloys were studied using gravimetric measurements and electrochemical potentiodynamic polarization method. As model corrosive environments 1N H_2SO_4, 1N NaCl and 1N NaOH solutions were used. The polarization measurements were carried out using a computerized potential-sweep technique (Princeton Corrosion Measurement System PAR with Soft Corr III software package) with a conventional three-electrode glass cell and a specially designed Teflon holder for the sample-electrode [10]. The potential-sweep rate of the polarization measurements was 1 mV/s. The potentials were measured against saturated calomel electrode (SCE). All measurements were performed at room temperature (25±2 ^{0}C).

RESULTS AND DISCUSSION

Structural characterization of the alloys

The XRD patterns of the as-quenched samples of both $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ and $Fe_{78}B_{13}Si_9$ alloys indicate basically an amorphous state (Fig. 1a and Fig. 2). The TEM micrographs of $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloy in as-quenched state have shown [12] the presence of a large number of nanocrystals (20-40 nm in size) uniformly dispersed in the amorphous alloy matrix, i.e. the structure of the alloy in as-quenched state is nanocomposite.

The heat treatment of the amorphous alloy samples at 700°C/3 h results in crystallization of both alloys and formation of multiphase microcrystalline structures composed by α-Fe, $Fe_3(Si,B)$ for $Fe_{78}B_{13}Si_9$ alloy and α-Fe, Co, $Fe_3(Si,B)$, Co_3Fe_7, $FeNi_3$, Ni_2Si_2 crystalline phases for $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloy (cf. Fig. 1b and Fig. 2).

Table 1. Electrochemical corrosion parameters of amorphous alloy $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ and $Fe_{78}B_{13}Si_9$ in different environments: corrosion potential (E_{corr}), corrosion current density (i_{corr}) and current density in the passive region (i_p).

Alloy	Environment	E_{corr}, mV(SCE)	i_{corr}, A/cm^2	i_p, A/cm^2
$Fe_{56}Ni_{18}Co_8B_{13}Si_5$	1N H_2SO_4	- 305	9,0.10^{-5}	-
	1N NaCl	- 235	1,0.10^{-5}	-
	1N NaOH	- 440	3,4.10^{-6}	5,5.10^{-5}
$Fe_{78}B_{13}Si_9$	1N H_2SO_4	- 480	2,5.10^{-3}	-
	1N NaCl	- 600	5,2.10^{-5}	-
	1N NaOH	- 490	2,6.10^{-5}	8,6.10^{-4}

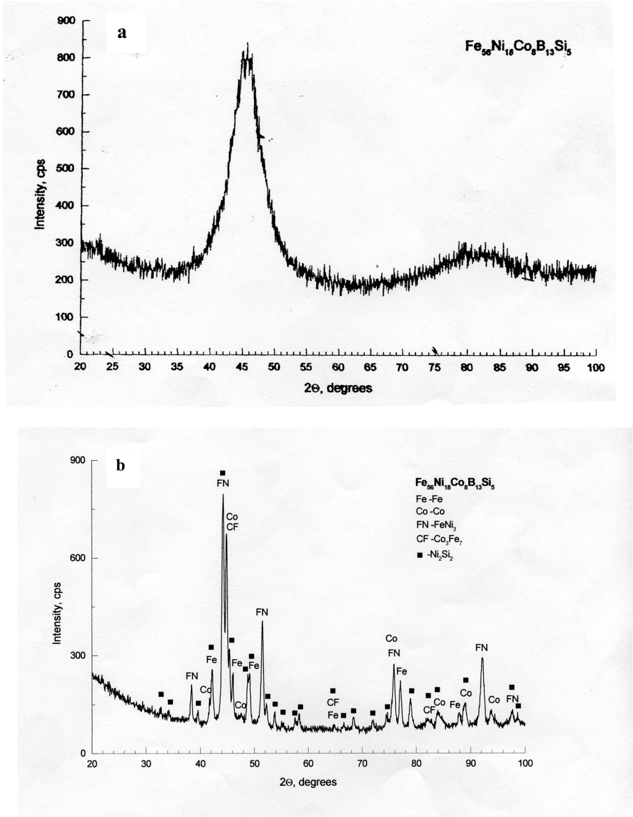

Fig. 1. XRD patterns of $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloys:a - as-quenched; b - heat treated at 700°C/3h.

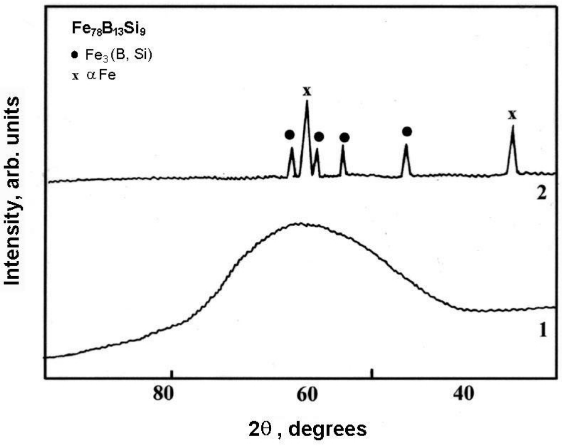

Fig. 2. XRD patterns of as-quenched (1) and heat treated at 700°C/3h (2) $Fe_{78}B_{13}Si_9$ alloys.

Electrochemical and corrosion behaviour of the alloys

Typical polarization dependencies E – log i for as-quenched samples of $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ and $Fe_{78}B_{13}Si_9$ alloys in the model corrosive environments of 1N H_2SO_4,

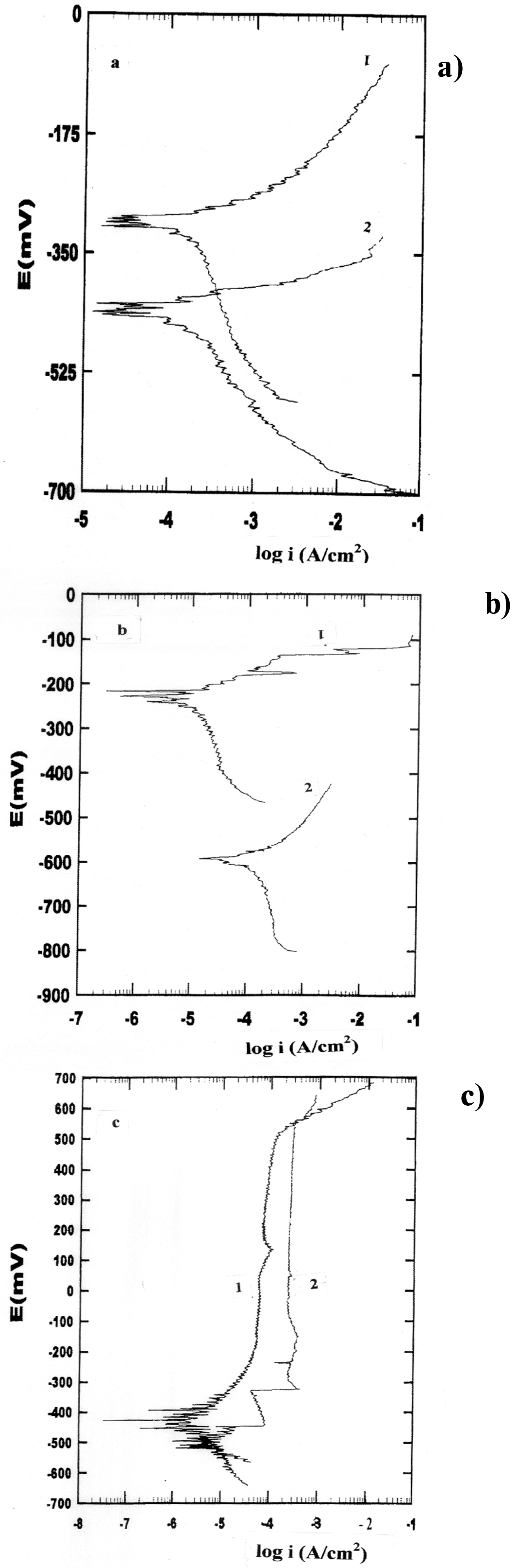

Fig. 3. Potentiodynamic polarization curves of amorphous $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ (1) and $Fe_{78}B_{13}Si_9$ (2) alloys in: a -1N H_2SO_4; b - 1N NaCl; c - 1N NaOH solutions.

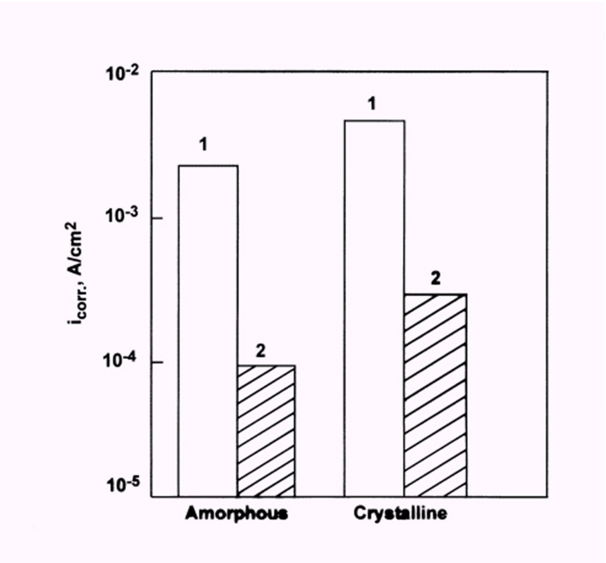

Fig. 4. Corrosion rates of amorphous and crystalline $Fe_{78}B_{13}Si_9$ (1) and $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ (2) alloys in 1N H_2SO_4.

1N NaCl and 1N NaOH solutions are shown in Fig. 3-a, b and c. The main electrochemical corrosion parameters obtained from polarization measurements are summarized in Table 1. As it seen, the corrosion rate of $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloy in all media studied is much lower (1-2 orders of magnitude) in comparison to that of the basic $Fe_{78}B_{13}Si_9$ alloy. Both alloys dissolve actively, although with different rates, in acidic and neutral media (cf. Fig. 3-a, b). In alkaline solution however both alloys show active to passive transition and anodic passivation in a wide potential region (about 1,0 V), but the anodic current density for $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloy is more than an order of magnitude lower. The polarization curves also suggest that the alloying with cobalt and nickel leads to considerable decrease of the rate of anodic metal dissolution reaction as well as to increase in susceptibility of the alloy to passivation and stability of its passive state. Thus, the double alloying of the basic Fe-B-Si alloy with nickel and cobalt results in a significant improvement of its corrosion resistance.

The crystallization of the amorphous alloys affects their corrosion behaviour in all cases but the effect depends greatly on the electrochemical properties of the crystalline phases formed [6,11,12,14]. It is to be expected that in case of activation controlled corrosion kinetics (e.g. corrosion of the alloys in acid solutions), the appearance of crystalline phases may affect significantly corrosion resistance of the alloys as shown for iron and nickel based alloys [6,14]. As it is seen from Fig. 4, both $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ and $Fe_{78}B_{13}Si_9$ alloys in amorphous state possess higher corrosion resistance in a sulfuric acid solution than their crystalline counterparts. The polarization measurements have shown that the crystallization of both alloys leads to considerable increase of the rate of anodic metal dissolution reaction, while the rate of hydrogen evolution reaction is affected only slightly. The lower corrosion rate of the alloys in as-quenched state is obviously related with their structural features – homogenious basically amorphous structure, uniformly distributed nanocrystals, absence of defined grain boundaries and other disorders characteristic for the crystalline state of metals (dislocations, kink sites, phase segregations, etc.). It sould be also noted that the favourable effect of alloying with nickel and cobalt on corrosion resistance of the Fe-B-Si alloy is more stronly express for the alloy in an amorphous (nanocomposite) state.

The data for the electrochemical properties of the crystalline phases formed during crystallization of the alloys studied however are largely missing in order to make a quantitative assertion of the machanisms for enhanced corrosion of the alloys upon their crystallization.

CONCLUSIONS

The alloying of Fe-B-Si alloy with nickel and cobalt improves considerably its corrosion resistance and the effect is more strongly expressed for the alloy in an amorphous state. The crystallization of amorphous $Fe_{78}B_{13}Si_9$ and $Fe_{56}Ni_{18}Co_8B_{13}Si_5$ alloys however results in decreasing of their corrosion resistance in acidic environment.

It is suggested that the higher corrosion resistance of the alloyed with cobalt and nickel amorphous alloys in respect to the basic Fe-B-Si alloy, together with the better magnetic and mechanical properties, is an additional stimulus for their practical application.

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