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MELT SPUN Fe-Co-Cr-B-Si ALLOYS CORROSION CHARACTERIZATION

Iulia SOLOMON[1], Nicolae SOLOMON[2]

Această lucrare prezintă rezultatele cercetărilor privind rezistenţa la coroziune a unui nou sistem de aliaje amorfe, Fe-Co-Cr-B-Si. Comportarea la coroziune a aliajelor amorfe, ca de altfel şi a aliajelor cristaline, poate fi determinată atât de factori interni (stuctura şi compoziţia chimică a aliajlului0), cât şi de factori externi (natura mediului agresiv, concentraţie, pH). Lipsa cristalinitaţii şi a defectelor specifice stării cristaline- limite de grăunţi, dislocaţii şi segregaţii, asigură aliajelor amorfe o înaltă rezistenţă la coroziune deşi termomecanic ele sunt metastabile.

Cercetările au fost realizate prin metoda gravimetrică pe benzi amorfe din sistemul de aliaje $Fe_{75-x}Co_xCr_1B_7Si_{17}$ obţinute prin metoda turnării pe rotitor. Ele au pus în evidenţă influenţa compoziţiei chimice, de exemplu - creşterea continuţului de Co, şi a mediului de lucru: 0.5N HCl, 1N HCl şi 1N H_2SO_4, asupra rezistenţei la coroziune. Cele mai bune rezultate s-au obţinut pe aliajul: $Fe_{65}Co_{10}Cr_1B_7Si_{17}$.

This paper presents the results of the research on the corrosion resistance of a new system of amorphous alloys, i.e. Fe-Co-Cr-B-Si. The corrosion behaviour of amorphous alloys as well as that of any other crystalline alloys may be determined both by internal factors (alloy structure and composition) and by external factors (aggressive medium type, concentration and pH-coefficient). The lack of crystallinity and of defects specific to the crystalline state -grain boundaries, dislocations and segregations ensure a high corrosion resistance to amorphous alloys in spite of being thermodynamically metastable. The research was performed through the gravimetric method on $Fe_{75-x}Co_xCr_1B_7Si_{17}$ amorphous alloy ribbons obtained by the melt-spinning technique. This research showed the influence of the alloy chemical composition, i.e. the increase of Co percentage, and working medium: 0.5N HCl, 1N HCl and 1N H_2SO_4 on corrosion resistance. The best results were recorded with: $Fe_{65}Co_{10}Cr_1B_7Si_{17}$.

Keywords: amorphous alloys, corrosion, X-ray diffraction

1. Introduction

Electrochemical interest in metallic glasses aroused since their appearance. In 1974 Naka, Hashimoto and Masumoto brought into evidence both the corrosion resistance and the inertness in various aqueous electrolytes [1]. It is believed that

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[1] Reader ,"Dunarea de Jos" University Galati, Romania, isolomon@ugal.ro

[2] Prof. "Stefan cel Mare" Suceava University, Romania, author for correspondence, nsolomon@usv.ro

all sources of localised corrosion disappear in the absence of common structural defects such as the grain boundaries, dislocations and segregations. Structure, chemical composition and material homogeneity are the factors influencing the electrochemical behaviour of amorphous alloys. Lack of sensitivity of an amorphous alloy to intergranular corrosion is apparently due to grain boundaries and segregations associated with them. A majority of amorphous alloys are passive in aqueous media. Considering the remarkable corrosion resistance of Fe, Ni, Co-based amorphous alloys it is important to explain the electrochemical action of non-metallic elements (P, B and Si) as well as their combination with alloying elements having a metallic character (Cr, Mo and W). This behaviour in the field of active dissolutions, in the active-passive transitional field as well as in that of the passivisation may be studied electrochemical by polarisation curves, gravimetry, electrochemical impedance, etc**.** Analysis of the surface by different methods allows the determination of the composition of passive layers and the distribution of the alloying elements. The effect of Cr on the corrosion resistance of amorphous alloys is higher than in the case of crystalline alloys [1]. The behaviour of Fe-Cr-P ternary alloys in aggressive media such as 1N HCl as compared to stainless steel is obvious. The efficiency of simultaneous alloying with Cr and P is superior to that of Cr and B and consequently should be emphasized. The $FeCr_{10}P_{13}C_7$ amorphous alloy passivates spontaneously in an aggressive medium. The passive film contains chromium hydroxide monohydrate. The previous studies showed [1-4] that the optimum enrichment in Cr in the case of passive films attains a maximum value with amorphous alloys showing 95% cations as compared with noticeable values in the case of conventional ferrite steels showing 58-75% cations. Comparison of the effect of other amorphizing elements underlines the special position phosphorus holds. In the case of steels including P, B or Si the above mentioned amorphizing elements cause the formation of a chromium borate or silicate which limits the percentage of this element available for the formation of the protective film of chromium hydroxide monohydrate.

2. Experimental procedure

Alloy ingots of $Fe_{75-x}Co_xCr_1B_7Si_{17}$ (where: x=1, 4, 7, and 10%Co) system were prepared from a mixture of pure Fe, Co, Cr, B and Si metals (purity $\geq$ 99.9%) by arc melting technique in a purified argon atmosphere. Amorphous alloy ribbons were obtained by the melt-spinning technique which consists in impinging a jet of molten alloy on the outer surface of a rotating copper wheel. The rotational speed of the dynamic equilibrated wheel was kept at 2100 rpm. X-rays diffraction analysis (Fig. 1) showed that the alloy is in an amorphous state [5].

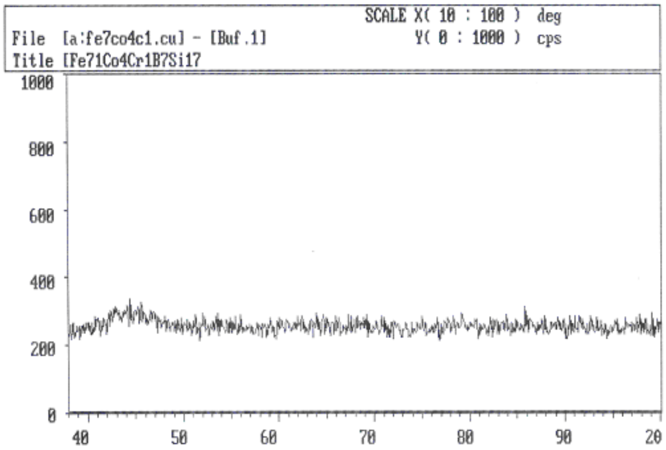


Fig.1. $Fe_{71}Co_4Cr_1B_7Si_{17}$ alloy X-ray diffraction diagram

The microhardness of the melt spun ribbons has been measured using Vickers method with a 50g load for comparative calculus.

In Fig. 2, it can be noticed that the microhardness of amorphous alloys increases with the increasing of Co percentage. It is probably due [5] to the formation of a more dense ribbon microstructure as a result of Co clusters formation prior to the commencement of melt quenching on the roller. The Co clusters induce their preferential cristalization in a phase rich in Fe and Cr. In this way the Co clusters act in the same way as an annealing heat treatment.

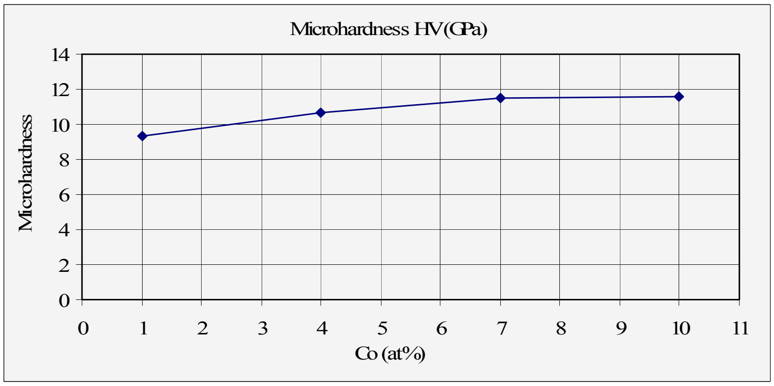


Fig.2. Microhardness versus Co content of the $Fe_{75-x}Co_xCr_1B_7Si_{17}$ amorphous alloys

The Co atoms presence assures the formation of a very compact microstructure consisting mainly of an amorphous phase mixed with a very fine nanostructure phase.

For corrosion behavior characterization the alloys were tested in order to find out the weight loss in three media, namely 1N H_2SO_4, 0.5N and 1N HCl. The losses were recorded for a 4 hour interval when weights were performed every 30 minutes. The corrosion rate for each time interval was determined by means of the following equation:

$$v_{cor} = \frac{\Delta m}{S \cdot t} \text{ x } 10^{-1} \qquad [\text{kg/m}^2 \cdot \text{h}] \qquad (1)$$

where:

v_{cor} – corrosion rate;
Δm– mass loss;
s – sample surface;
t – test duration,

and penetration coefficient:

$$i_p = \frac{v_{cor}}{\rho} \text{ x} \cdot 8.76 \cdot 10^{-3} \qquad [\text{m/year}] \qquad (2)$$

where:

ρ - material density.

The samples were very thin ribbons with thickness between 25 and 32 μm and 2 mm width, having a very large surface in contact with the corrosive agent. Before being weighed with a digital analytical balance, samples were degreased in acetone, washed in distilled water and then dried in air. Electrolytes of 1N H_2SO_4, 0.5 N HCl and 1N HCl solutions open to air were used at room temperature (about 298 K). Mass loss of the amorphous alloys ribbons after immersion in the above mentioned solutions was measured for estimating the corrosion rates. After the immersion test, surfaces of the alloy specimens were observed by optical microscope.

3. Results and Discussion

In this section some of the experimental research results regarding to the corrosion resistance of the above mentioned alloys will be presented. The air side surface (freely solidified) and the wheel side surface (solidified in contact with the rotating support) of the amorphous ribbons were studied under an optical microscope. The wheel side surface shows very small air pockets randomly distributed with varying size produced by gases entrapped by the liquid metal jet during the production process. The samples also show asperities (roughness) on

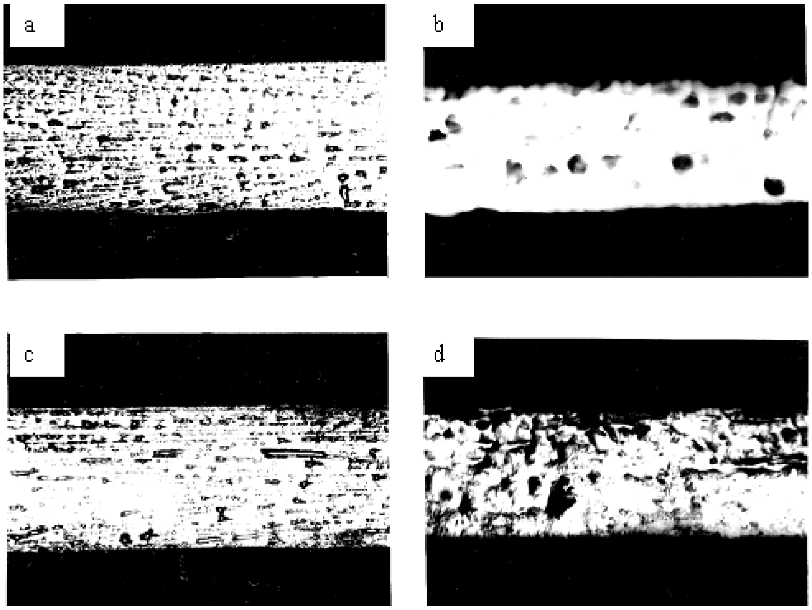
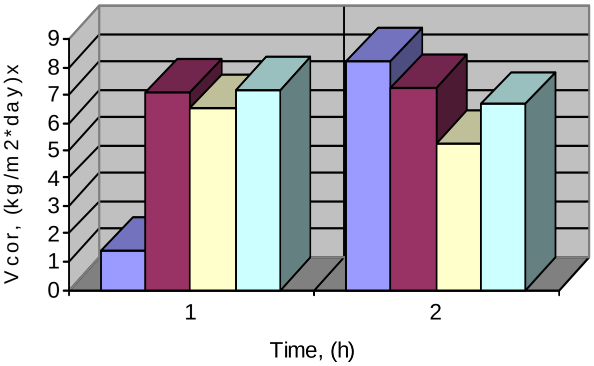


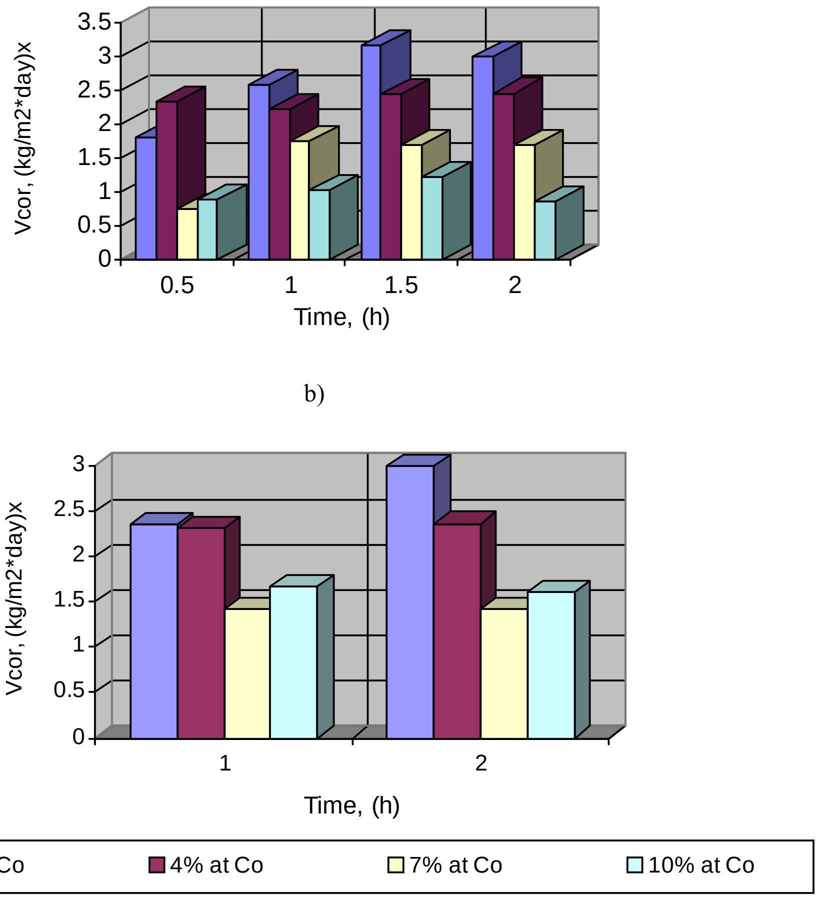
Fig.3. Surface morphology of the $Fe_{71}Co_4Cr_1B_7Si_{17}$ amorphous ribbons (a, c) wheel side and (b, d) air side surfaces (a, b) before and (c, d) after corrosion

the air side surface [6]. Fig. 3, obtained by optical microscope shows the above stated aspects.

The sample surfaces were also analyzed after the corrosion test. The ribbon surface contacting the rotating support shows a higher corrosion resistance than the surface in the opposite side. This can be explained by the cooling process of these two surfaces at different cooling rates during the solidification process.



a)



b)

c)

Fig.4. Histograms showing the dependence of corrosion rate of $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys in (a) 1N H_2SO_4, (b) 1N HCl and (c) 0.5N HCl media versus the cobalt content

Due to a lower cooling rate of the air side surface crystalline nuclei could form, but this process was not confirmed through the X-ray diffraction [7]. The present study has been performed in order to investigate the effect of increasing of cobalt content on the corrosion resistance of the series of $Fe_{75-x}Co_xCr_1B_7Si_{17}$ amorphous alloys.

The histograms of Fig. 4 show the dependence of corrosion rate of $Fe_{75-x}Co_xCr_1B_7Si_{17}$ alloys in (a) 1N H_2SO_4, (b) 1N HCl and (c) 0.5N HCl solutions versus the cobalt content. The variation of corrosion resistance expressed by the penetration coefficient can be noticed in Fig.5.

The amorphous metallic alloys are thermodynamically instable. The corrosion behaviour in the case of the amorphous alloys as well as in that of any crystalline alloys may be influenced both by internal factors (the alloy composition, the type of the components, the presence of the metalloids) and by external ones (aggressive medium pH-coefficient and composition). Irrespective of the corrosive medium, the amorphous alloys have a better and better behaviour proportionally with increasing cobalt content, which is obvious in Figs 4-5.

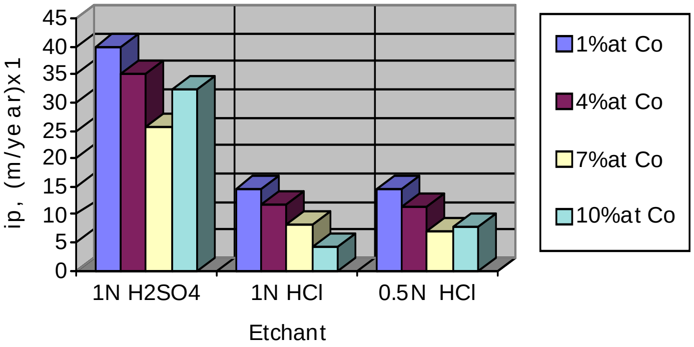


Fig.5. Variation of penetration coefficient depending on the cobalt concentration and the nature of the aggressive medium

This effect may be explained by the behaviour of cobalt itself. Cobalt may be considered a somehow noble metal characterized by a low corrosion rates in neutral aqueous solutions, without oxidants, and a low corrosion rate in acid solutions. The studies performed by Angelini and her collaborators [1] indicate a tendency of cobalt to become passive in the presence of water through the appearance of an oxide film. In the case of some mixtures having a high percentage of iron, the reaction of non-adherent products typically produced by this metal results in a continuous weight loss of the sample.

Better corrosion resistance of amorphous alloys than crystalline alloys can be explained at least by two reasons. First of all corrosion resistance is intimately related to both the chemical composition of the alloys and their structure. It is known that in the case of crystalline alloys, mono-phase alloys have a better corrosion resistance than bi or multi phases alloys. Also, in the case of crystalline structure corrosion often occurs preferentially at grain boundaries and second phase particles. Good corrosion resistance of single phase metallic alloys is often attributed to structural and compositional homogeneity.

Metallic amorphous alloys are free from such metallurgical features such as grain boundaries and second phase. Also the good corrosion resistance of amorphous alloys is linked to the ability of these alloys to form supersaturated solid solution in one or more alloying elements. These alloying elements available in solid solution may be incorporated into the oxide film to enhance its passivity.

At high percentage the cobalt forms of a shallow protective film, probably a more or less hydrated oxide, which prevents further corrosion [8-10]. Quantitative analysis of the elements dissolved in 0.5 N and 1N HCl solutions revealed the following (see Figs.3b and 3c):

(1) In more aggressive solutions alloys with low Co content the dissolution rates are close to those of the nominal alloys (i.e. $Fe_{74}Co_1Cr_1B_7Si_{17}$)

(2) In almost neutral solutions alloys with high Co content the dissolution rates are perceptibly different from those of the nominal compositions.

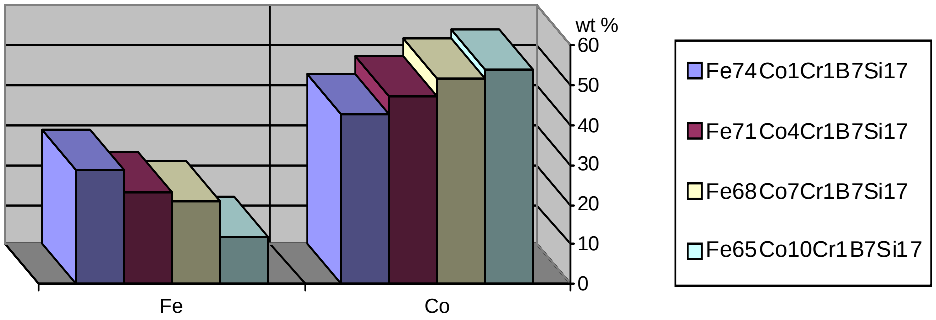


Fig.6. Variation in iron and cobalt dissolved in the 0.5N HCl etchant

Fig. 6 shows the results of quantitative analysis for iron and cobalt dissolved in the 0.5N HCl solution. The data in the table related to the total weight losses during the corrosion process, refer only to the iron and cobalt percentage variation as components of the $Fe_{75-x}Co_xCr_1B_7Si_{17}$ amorphous alloys. In the analysed case of 0.5N HCl solution the dissolved iron percentage decreases with increasing of cobalt content, but in the same time the cobalt content in 0.5N HCl solution increases with its increasing percentage in the amorphous alloys composition.

The present study underlines the importance of the corrosive medium and its concentration. The Fe-Co-Cr-B-Si alloys displayed inferior corrosion resistance in sulphuric acid and its penetration coefficient ranges between 20 and 40 mm/year, as compared to their behaviour in hydrochloric acid in which the penetration coefficient is between 4 and 14 mm/year. When the samples were kept in 1N hydrochloric acid for four hour practically the penetration coefficients are identical with those kept in 0.5N hydrochloric acid for two hour. The passivation of amorphous alloys increase with increasing of HCl concentration.

4. Conclusions

Taking into account the above mentioned results the following conclusions can be drawn:

-$Fe_{75-x}Co_xCr_1B_7Si_{17}$ amorphous ribbons improve their corrosion behavior with increasing of the alloys Co percentage. At high percentage the cobalt forms a thin protective film which prevents further corrosion.

-Ions type and concentration in the corrosive medium as well as the solution pH have an impact on the corrosion rate of amorphous metallic alloys.

-The corrosion resistance of the ribbons in the hydrochloric acid environments varies with solution concentrations. The penetration coefficients are identical when samples were kept in 1N HCl for 4 hour test with those recorded when samples were kept for 2 hour test in 0.5N HCl. It means that the amorphous alloy becomes more passive when the HCl concentration increases.

-The ribbon wheel side surface shows a higher corrosion resistance than the surface in the opposite side. This behaviour is the result of some structural differences between air side (free of grain boundaries, second-phase particles) and wheel side ribbon surfaces due to the cooling process at different cooling rates.

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