

The Effect of Chromium on the Corrosion Resistance of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ Amorphous Alloys

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As respostas voltamétricas de ligas amorfas de $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}$ em solução de KOH 0,5 N foram estudadas a temperatura ambiente. Os resultados mostram, no intervalo de potencial onde a camada passivante é formada, características que são qualitativamente similares àquelas relacionadas à voltametria do ferro em meios alcalinos. A adição de cromo à liga amorfa de $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}$ é eficaz para melhorar a resistência à corrosão. Quando o conteúdo de cromo da liga amorfa de $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ é 4% at., a ciclagem de potencial não produz praticamente nenhuma alteração na forma dos voltamogramas e a espessura do filme diminui. Os filmes passivos formados sobre as ligas amorfas de $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ mostram alta resistência à corrosão por pite em solução de KOH 0,5 N + KCl 0,5 N. Medidas de polarização mostram que a adição de 4% at. de cromo reduz de modo significativo a corrente de dissolução ativa em solução de HCl 2 N.

The voltammetric responses of $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}$ amorphous alloys in 0.5 N KOH solution was studied at room temperature. In the potential range where the passivating layer is formed, the results show features which are qualitatively similar to those referring to iron voltammetry in alkaline media. The addition of chromium to $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}$ amorphous alloys is effective in improving the corrosion resistance. When the chromium content of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ amorphous alloys is ≥ 4 at. % the potential cycling produces practically no changes in the shape of the voltammograms, and the passive film thickness decreases. The passive films formed on the $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ amorphous alloys show high resistance to pitting corrosion in 0.5 N KOH + 0.5 N KCl solution. Polarization measurements show that the addition of ≥ 4 at. % of chromium significantly decreases the active dissolution current in 2 N HCl solution.

Key words: *amorphous alloys, corrosion, passivation*

Introduction

Rapid solidification from the melt is known to produce amorphous alloys with remarkably high corrosion resistance. The corrosion resistance for the majority of metals is determined by the chemical stability and uniformity of the protective corrosion film product. High corrosion resistance is provided by rapid passivation and high concentration of beneficial elements in the passive film. Both of these two factors are affected by the activity of the alloy¹.

Passive films formed on corrosion resistant amorphous and crystalline alloys containing chromium are composed mainly of hydrated chromium oxihydroxide, $\text{CrO}_x(\text{OH})_{3-2x} \cdot n\text{H}_2\text{O}$, and the surface film with a higher concentration of hydrated chromium oxihydroxide is more protective². The high reactivity of amorphous alloys is responsible for the

high degree of chromium enrichment in the passive film, and their chemically homogeneous nature provides high passivating ability and corrosion resistance.

In the present study, the corrosion behavior of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ amorphous alloys was examined. In order to clarify the role of chromium on the electrochemical response of anodically formed oxide layers on amorphous alloys, with and without chromium, voltammetric responses in alkaline solutions were compared. Pitting resistance of the passive films formed was evaluated in 0.5 N KOH + 0.5 N KCl solutions. The corrosion tests were made at 20 mV s^{-1} between $E_c = -1.2 \text{ V}$ and $E_A = +0.8 \text{ V}$, followed by a potential holding at E_A during 60 s. In order to study the corrosion resistance of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ amorphous alloys potentiodynamic polarization measurements were carried out in 2 N HCl.

Experimental

Alloy ingots were prepared by arc melting in a water cooled copper crucible with He. From these ingots, amorphous alloy ribbons of about 5 mm in width and 20-30 μm thick were prepared by the Planar Flow Casting method. The ribbon compositions were determined by electron probe microanalysis. The amorphous structure of the samples was confirmed by X-ray diffraction. Prior to the electrochemical measurements, the amorphous alloy ribbons were degreased in acetone and rinsed with distilled water.

The electrochemical measurements were made in a typical three-electrode cell. Working electrodes consisting of 2 cm^2 wide amorphous alloy ribbons were used. Electrode potentials were measured against a Ag/AgCl reference electrode with a built-in electrolyte bridge to prevent chloride ion diffusion into the electrolyte solution. A platinum sheet was employed as the counter electrode. An 0.5 N KOH aqueous solution was employed as the electrolyte. The experiments were made at room temperature, and the potentials were controlled with a Princeton Applied Research Model 273 potentiostat.

The electrochemical behavior of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_{x(0 \rightarrow 5)}$ amorphous alloys was evaluated by the voltammetric technique. A cleaned ribbon, with a surface area of 2 cm^2 was treated to repetitive triangular potential sweeps (RTPS) between $E_C = -1.7$ V and $E_A = +0.2$ V at 20 mV s^{-1} . The voltammograms obtained from this procedure were compared in order to evaluate the influence of chromium on the oxide film growth.

The pitting corrosion resistance of the specimens was evaluated by corrosion tests in 0.5 N KOH + 0.5 N KCl solution. The corrosion tests consisted of a potential sweep between $E_C = -1.2$ V and $E_A = +0.8$ V at 20 mV s^{-1} , followed by a potential holding at E_A for 60 s.

The corrosion behavior of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_{x(0 \rightarrow 5)}$ amorphous alloys was evaluated by potentiodynamic anodic polarization. Polarization curves were measured with a potential sweep rate of 20 mV min^{-1} .

Results and Discussion

The repetitive triangular potential sweeps of the $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}$ amorphous alloys run in 0.5 N KOH solution between $E_C = -1.7$ V and $E_A = 0.1$ V at 20 mV s^{-1} show the anodic and cathodic current contributions during the scan (Fig. 1). The voltammograms continuously modify during cycling as indicated by the arrows. The increase of the voltammetric charge indicates the accumulation of the anodically formed surface layer during cycling. The increase of the voltammetric charge is principally related to the pair of peaks III-III and IV-IV. This voltammogram exhibits an additional contribution indicated by I, II and V. This description of the voltammogram is qualitatively similar to the voltammetric response of iron in alkaline media³⁻⁵.

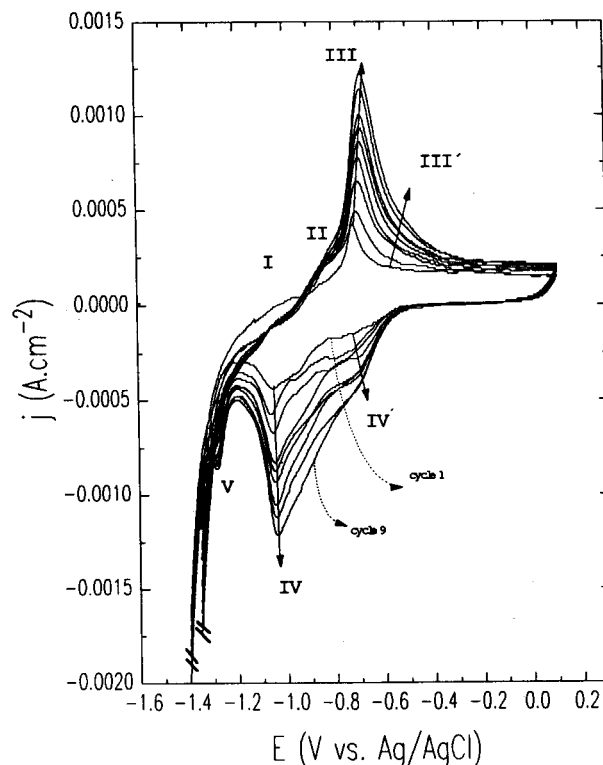


Figure 1. Repetitive voltammograms run in 0.5 N KOH at 20 mV s^{-1} between $E_C = -1,700$ mV, $E_A = +100$ mV. The 1st to 9th cycle are shown.

The voltammetric responses of the $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_{x(0 \rightarrow 5)}$ amorphous alloys, run under comparable conditions are indicated in Fig. 2. The reduction of the voltammetric charge is clearly visible, decreasing the charge accumulation related to the pair of peaks III-III and IV-IV. When the chromium content is ≥ 4 at. % the voltammograms recorded after potential cycling are slightly different from the first voltammogram, and accordingly no charge accumulation was noticed.

Thick oxide layers were obtained when the $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}$ amorphous alloys were subjected to the RTPS treatment in alkaline solutions. Control voltammograms were obtained after the RTPS treatment recorded single triangular potential sweeps between $E_C = -1.2$ V and $E_A = +0.2$ V at 200 mV s^{-1} (control variables). The influence of the electrochemical variables on the formation and growth of the surface oxide layer in 0.5 N KOH solution at room temperature may be followed by checking the anodic charge voltammetric of the control voltammograms (Fig. 3). The experimental procedure was essentially the same as that previously described^{6,7}. It was found that the optimum values, or maximum efficacy, of the oxide layer growth were between $E_{C\text{opt}} = -3.2$ V and $E_{A\text{opt}} = +0.1$ V at $v_{\text{opt}} = 1$ V s^{-1} .

The anodic voltammetric charges of the $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_{x(0 \rightarrow 5)}$ amorphous alloys, obtained with optimum electrochemical conditions, are shown in Fig. 4.

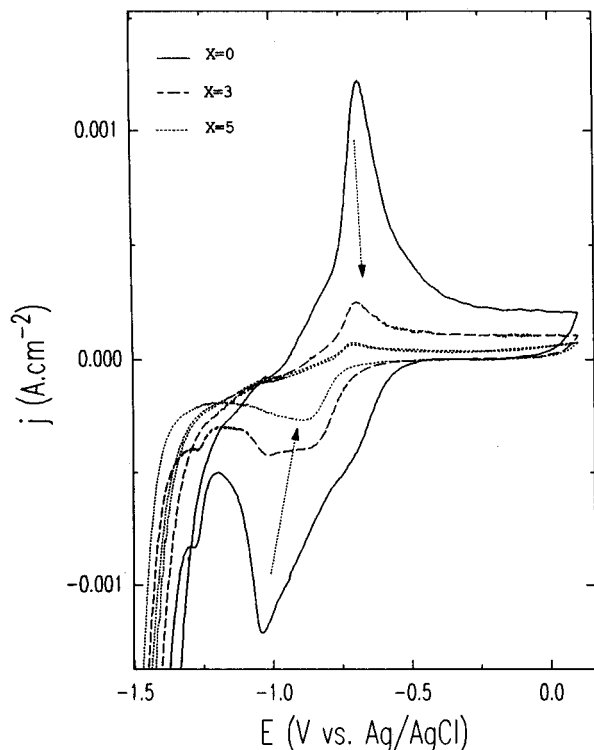


Figure 2. Comparative voltammograms run in 0.5 N KOH solution at 20 mVs^{-1} between $E_C = -1.7 \text{ V}$ and $E_A = +0.2 \text{ V}$. The 9th cycles are shown.

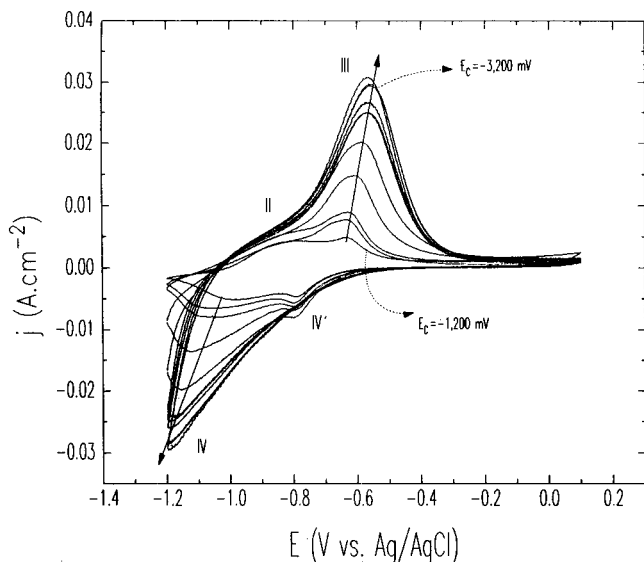


Figure 3. Control voltammograms run in 0.5 N KOH at 200 mVs^{-1} between $E_A = +100 \text{ mV}$ and different E_C (range $-1,200$ / $-3,200 \text{ mV}$).

This charge indicates the accumulation of the anodically formed surface layer during cycling. The addition of chromium remarkably decreases the anodic voltammetric charges. Therefore, these results confirm the rapid formation of a passive film with high uniformity when the Cr-content is increased. When the chromium content was ≥ 4 at. %, the treatment efficiency is practically constant when the number of cycles is above 200, independent of the

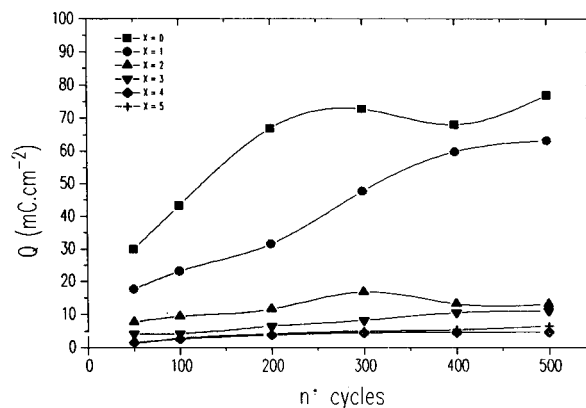


Figure 4. Anodic voltammetric charge vs. treatment time plots obtained in 0.5 N KOH solution between $E_C = -3.2 \text{ V}$ and $E_A = +0.1 \text{ V}$ at 1 V s^{-1} .

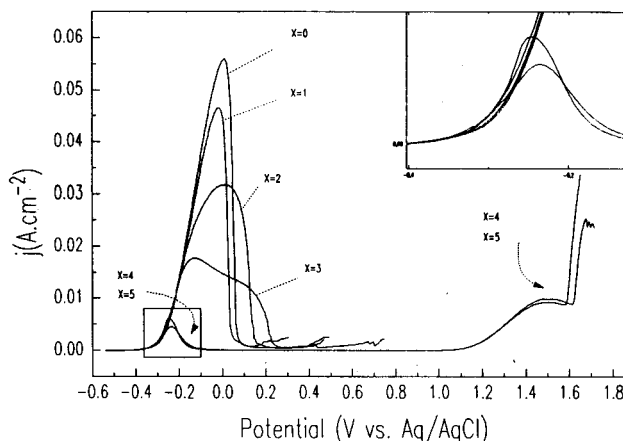


Figure 5. Potentiodynamic polarization curves of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ amorphous alloys measured in 2 N HCl at room temperature.

chromium content. An independence similar to that mentioned above has been obtained in stainless steel with 18 at. % chromium content⁸.

Figure 5 shows the potentiodynamic polarization curves of the $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_x(0 \rightarrow 5)$ amorphous alloys measured in a 2 N ClH solution at room temperature. Amorphous alloys containing ≤ 3 at. % of chromium show a high active dissolution current. When the chromium content is ≥ 4 at. % the amorphous alloys show a low active current density, with the consequent formation of a passive film.

The corrosion test of amorphous alloys covered with oxide films are shown in Fig. 6. Oxide films were generated between $E_C = -3.2 \text{ V}$ and $E_A = +0.2 \text{ V}$ at 1 V s^{-1} in 0.5 N KOH solution after running 200 potential cycles. It should be noted that the voltammetric response of the samples, after the potential holding, shows no additional contributions during a reverse scan. These results suggest that the oxide layers generated on the surface are not only stable in the medium where they were generated, but also in corrosive media.

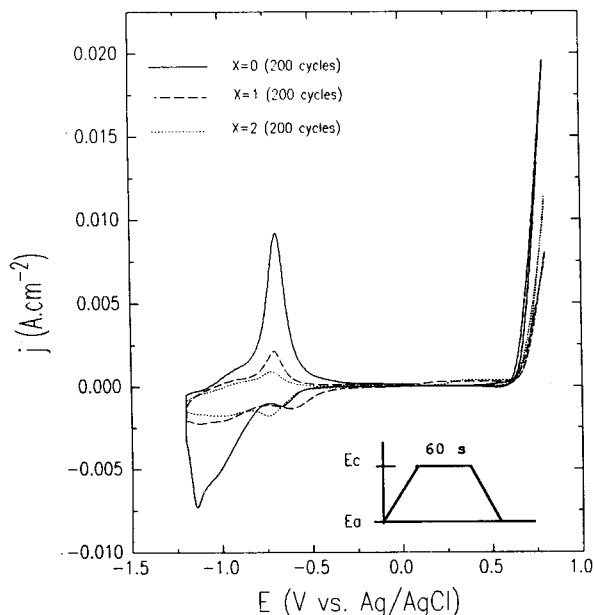


Figure 6. Corrosion test plots of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_{x(0 \rightarrow 5)}$ amorphous alloys measured in 0.5 N KOH + 0.5 N KCl solution, measured between $E_C = -1.2$ V and $E_A = +0.8$ V at 20 mV s^{-1} , with a potential holding of 60 s at E_A potential.

Conclusions

This work permits the following conclusions:

1. Scanning the rate potential of the electrode permits oxide layers to be developed with behavior similar to that of other Fe-based amorphous alloys.
2. When the chromium content of $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_{x(0 \rightarrow 5)}$ amorphous alloys is ≥ 4 at. % the passive film thickness remarkably decreases.

3. The best corrosion behavior was found in the $\text{Fe}_{69.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_4$ and $\text{Fe}_{68.5}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_5$ amorphous alloys with typical potentiodynamic polarization curves for materials in a passive state.

4. The $\text{Fe}_{(73.5-x)}\text{Cu}_1\text{Nb}_3\text{B}_9\text{Si}_{13.5}\text{Cr}_{x(0 \rightarrow 5)}$ amorphous alloys with a generation of layers of maximum thickness substantially improve pitting resistance in comparison to the control specimens in a reception state.

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