



## Comparison of the corrosion resistance behaviour for two metal-metal glassy alloys in neutral solution with chloride impact



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### ABSTRACT

The electrochemical behaviour of bulk glassy Fe<sub>78</sub>Co<sub>9</sub>Cr<sub>10</sub>Mo<sub>2</sub>Al<sub>1</sub> and Fe<sub>49</sub>Co<sub>49</sub>V<sub>2</sub> alloys was investigated using electrochemical techniques with different concentrations of Na<sub>2</sub>SO<sub>4</sub> solution (0.25, 0.5 and 1.0 M). The alloys surfaces were characterized by various morphology and composition techniques. The corrosion rate of the two alloys is inversely proportional to the concentration of Na<sub>2</sub>SO<sub>4</sub> solution. The VX9 alloy exhibited spontaneous production of a good passive layer in Na<sub>2</sub>SO<sub>4</sub> solutions as a response to the presence of protective elements, such as Cr (10%), Mo (2%) and Al (1%). No passivation occurred on the surface of the VX50 alloy, with only salt precipitating on it. Adding chloride reduces the resistivity of both alloys as it is a localized attack.

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### 1. Introduction

The bulk metallic glasses (BMGs) are particularly important because these materials are formed through the very rapid cooling of the liquid metal with suppression of the nucleation process to obtain an amorphous structure that differs from the usual crystallization structure [1]. The Fe-based bulk metallic glasses (BMGs) are useful as engineering, magnetic, structural and surface coating materials in industrial applications due to their relatively low cost. Fe-based BMGs with amorphous structures have unique physical and chemical properties, including high strength, a large elastic strain limit and excellent wear and corrosion resistance. Furthermore, these BMGs have other remarkable engineering properties, such as good ductility, high toughness and inherent brittleness. There is potential for Fe-based BMGs to be used as a functional and structural material in applications due to these outstanding properties [2–6]. Metallic glass was first discovered in the Au-Si alloy system by Duwez in 1960 [7]. In general, metallic glasses can be sorted into two groups: metal–metalloid-based glasses and metal–metal-based glasses. BMGs in metal–metal systems were first

prepared in the early 1990s by the stabilization of supercooled liquid [8–10]. This was used for the production of some industrial products due to the excellent properties of Ni-based, Fe-based and Ti-based bulk metallic glasses, which were investigated by Nobuyuki Nishiyama [11]. Fe-Co-based alloys are an important bulk glassy alloy. These alloys exhibit very interesting mechanical, thermal, magnetic and other properties [12]. Fe-based BMGs are attractive in the industrial field due to their commercial importance [13] and unique combination of ultra-high strength [14], excellent soft magnetic properties [15], good corrosion resistance [16] and relatively low preparation costs [17]. Fe<sub>78</sub>Co<sub>9</sub>Cr<sub>10</sub>Mo<sub>2</sub>Al<sub>1</sub> and Fe<sub>49</sub>Co<sub>49</sub>V<sub>2</sub> BMGs were tested by immersion tests and electrochemical measurements in artificial acid rain. This study investigated the passivation behaviour of both alloys for different immersion times. They found that the alloys have higher resistivity when exposed to the artificial solution for a longer period of time due to the corrosion products acting as a protective layer to protect the surface [18]. Researchers have also studied BMGs in different types of solution, such as neutral [19], acidic [20] and basic [21] solutions. Adding the Fe to Co-based metallic glasses may result in the enhancement of magnetic properties and glass forming ability (GFA) [22]. After being placed in 0.1 M Na<sub>2</sub>SO<sub>4</sub>, the Fe<sub>44.3</sub>Cr<sub>5</sub>Co<sub>5</sub>Mo<sub>12.8</sub>Mn<sub>11.2</sub>C<sub>15.8</sub>B<sub>5.9</sub>)<sub>98.5</sub>Y<sub>1.5</sub> glassy alloy had an insignificant weight loss after 100 days, which showed the high resistance of the

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alloy in this solution due to weight gains. This was attributed to the formation of corrosion products on the surface of the alloy [16].

The aim of this present study is to elucidate the electrochemical behaviour of VX9 and VX50 alloys in different concentrations of Na<sub>2</sub>SO<sub>4</sub> solution. Furthermore, we aimed to investigate the impact of chloride on this behaviour to expand the knowledge of Fe-Co-based BMGs and encourage their easy implementation in industrial applications.

## 2. Experiment materials and methods

Fe<sub>78</sub>Co<sub>9</sub>Cr<sub>10</sub>Mo<sub>2</sub>Al<sub>1</sub> and Fe<sub>49</sub>Co<sub>49</sub>V<sub>2</sub> were provided by Vacuum-schmelze. The electrochemical measurements of these two alloys were obtained using three electrodes (saturated Ag/AgCl electrode, a platinum counter electrode and the sample), which was provided by Gamry Instruments, USA (potentiostat/galvanostat-Interface 1000™). They were encapsulated by temperature-resistant resin aside from a working area of 1 cm<sup>2</sup>, which would be subsequently exposed to the aerated Na<sub>2</sub>SO<sub>4</sub> solution at 27 °C.

The electrochemical measurements in Na<sub>2</sub>SO<sub>4</sub> solution were obtained after a stabilization period for 1 h at open circuit potential with an applied 10-mV as sine wave being the excitation signal from peak to peak in extended from 800 kHz to 0.1 Hz. After the impedance run, the cyclic polarization measurements were obtained with a potential forward sweep from the cathodic to the anodic direction (–500 mV–1200 mV for VX9 and –800 mV to 1200 mV for VX50) and a potential reverse sweep from anodic to cathodic direction in the same range at a scan rate of 1.5 mV/s.

The structure and morphology of the alloy surfaces were characterized by using XPS analysis with AlKα at 150 W of X-ray power (Kratos Axis Ultra DLD), scanning electron microscope (SEM; Superscan SS-550, Shimadzu company, made in Japan) and AFM (digital instrument CP-II, Veeco company, made in USA) techniques in neutral media.

## 3. Results and discussion

### 3.1. Electrochemical impedance spectroscopy measurements (EIS)

The Nyquist and Bode plots of the VX9 and VX50 alloys at different concentrations of (0.25, 0.5 and 1.0 M) Na<sub>2</sub>SO<sub>4</sub> solution are shown in Fig. 1(a–d), respectively.

The Nyquist plots for the VX9 alloy shown in Fig. 1(a) show the one-time constant corresponding to one capacitive arc at high frequencies and one peak in the phase angle plot at 0.25 M with the diffusion tail at a low frequency. Increasing Na<sub>2</sub>SO<sub>4</sub> concentration will create another capacitive arc, which has a diffusion tail at low frequencies with 0.5 and 1.0 M Na<sub>2</sub>SO<sub>4</sub>. The appearance of the additional capacitive loop when moving towards the low frequency is the result of the production of a passive layer that corresponds with a broad peak of the phase angle (Fig. 1(c)).

The presence of one capacitive arc and one peak in the phase angle plots at the high frequencies for VX50 alloy (Fig. 1(b,d)) indicates that the dissolution process is dominant in Na<sub>2</sub>SO<sub>4</sub> solutions. Generally, for both two alloys, the diameter values of the capacitive arc in Nyquist plots increased with an increase in the concentration of Na<sub>2</sub>SO<sub>4</sub> solution from 0.25 to 1.0 M.

To study the influence of chloride ion concentration (0.001, 0.01 and 0.1 M) on the localized corrosion of VX9 and VX50 alloys, the 1.0 M Na<sub>2</sub>SO<sub>4</sub> solution was chosen. This concentration was chosen due to the maximum diameter of the charge transfer resistance ( $R_{ct}$ ) obtained for both alloys. The obtained Nyquist and Bode plots for VX9 and VX50 alloys are shown in Fig. 1(e,f) and (g,h), respectively. The fitting data obtained by the analysis of the impedance spectra are summarized in Tables 1 and 2 (with the Chi-square ( $\chi^2$ ))

of about 10<sup>–3</sup>–10<sup>–4</sup>). The Warburg impedance  $Z_W$  can be presented according to a previous study [23] as follows:

$$Z_W = \sigma \omega^{-1/2} (1 - j) \quad (1)$$

$$\text{In which } \sigma = \frac{RT}{z^2 F^2 A \sqrt{2}} \left( \frac{1}{C^o \sqrt{D_o}} + \frac{1}{C^R \sqrt{D_R}} \right),$$

where  $\sigma$  is the Warburg coefficient ( $\Omega \text{cm}^2 \text{s}^{-1/2}$ );  $\omega = 2\pi f$  ( $\text{rad.s}^{-1}$ );  $R$  is the universal gas constant;  $F$  is the faraday constant;  $T$  is the temperature;  $A$  is the area of the working electrode;  $z$  is the charge number;  $C^o$  is the concentration of the oxidant;  $D_o$  is the diffusion coefficient of the oxidant;  $C^R$  is the concentration of the reductant; and  $D_R$  is the diffusion coefficient of the reductant.

There is the appearance of the diffusion tail at 0.25 M Na<sub>2</sub>SO<sub>4</sub>, which begins to overlap with the capacitive arc for VX9 alloy. This is due to the value of  $\sigma$  being equal to value of  $R_{ct}$  with an angle of approximately 45° to the real axis. The value of  $\sigma$  increased and there is increasing overlap with the diffusion tail remaining at 45° (Fig. 1(a)). The diffusion tail completely distorts the semi-circular shape, which creates an angle that is greater than 45° to the real axis. This phenomenon occurs at 0.5 and 1.0 M due to the value of  $\sigma$  being significantly greater than  $R_{ct}$ , which indicates that the diffusion processes occur slower than the metal charge–transfer reaction [23]. The behaviour of the single capacitive arc at 0.25 M Na<sub>2</sub>SO<sub>4</sub> was attributed to the charge transfer control and double layer capacitance at the metal/solution interface at a high frequency and the diffusion control at a low frequency (the slowest process as shown in Table 1). The end of the diffusion tail shifts to the left with an increase in the concentration of the Na<sub>2</sub>SO<sub>4</sub> solution, which reflects the increasing corrosion resistance.

The diffusion tail does not appear at low frequencies for VX50 alloy (Fig. 1(b)). This means that the value of  $\sigma$  is equal to zero [23]. The impedance plots of the VX50 alloy are explained by using the one-time constant, which is related to the one process that occurred on the alloy surface (dissolution process). The one capacitive arc produced represents the combined effects of electric double layer capacitance and charge transfer resistance.

There is a larger diameter of the capacitive loops with an increase in the concentration of Na<sub>2</sub>SO<sub>4</sub> solution. This suggests the presence of an electric double layer capacitance at the electrode/solution interface, where the maximum value of the double layer capacitance is obtained at the lowest arc diameter for the two alloys at a concentration of 0.25 M. On the other hand, the diameter of the capacitive arc for VX9 alloy in all concentrations of Na<sub>2</sub>SO<sub>4</sub> solution is much larger than the VX50 alloy. The resistance of the two alloys is related to the magnitude of charge transfer resistance,  $R_{ct}$ , at the metal/solution interface (Table 1). The resistance of VX9 alloy is also related to the dielectric properties of a thin passive film that formed on it. This passive film enhances the resistance of the alloy due to the inclusion of Cr<sub>2</sub>O<sub>3</sub>, MoO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. These compounds are considered to be p-type semiconductors. Furthermore, this passive film also contains a high amount of Fe<sub>2</sub>O<sub>3</sub>, which is classified as a n-type semiconductor [24]. This passive film acts as a diffusion barrier against alloy dissolution. The resistance of VX9 alloy ( $15.12 \times 10^3 \Omega \text{cm}^2$ ) is about nine times higher than the resistance of VX50 alloy ( $1.67 \times 10^3 \Omega \text{cm}^2$ ) in 0.25 M Na<sub>2</sub>SO<sub>4</sub> solution, which demonstrates the outstanding resistance of VX9 alloy in Na<sub>2</sub>SO<sub>4</sub> solution. Furthermore, the values of  $Q_{f/s}$  for VX9 alloy are much lower than the values of  $Q_{f/s}$  for VX50 alloy, which is related to the formation of a protective layer on VX9 alloy in Na<sub>2</sub>SO<sub>4</sub> solution. The n-values (0.89) illustrated in Table 1 indicate the CPE(Q) is associated with the film capacitance processes.

From Fig. 1 (e,f) and Table 2, the increase in the concentration of

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