Research Article

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Assessment of Energy Efficiency of High Entropy Metallic Glasses in Aqueous Solutions

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Abstract
A developed criterion of the energy efficiency of iron-boron-silicon, i.e., high entropy, metallic glasses was implemented in hydrochloric acid solutions. The criterion; lim (the conductivity of the metallic glass in aqueous solution to the conductivity of the metallic glass in air) =1 was applied to determine the energy efficiency of the metallic glass in the aqueous solution when the conductivity of a metallic glass in air became equal (decreased) to the steady conductivity of the metallic glass in aqueous solution as a function of time of the exposure of the metallic glass to the aqueous solution. This criterion was used to determine the energy efficiency of metallic glasses with a wide range of hydrochloric acid concentration. The values of the conductivities were determined by the electrochemical impedance spectroscopy (EIS). In addition, the criterion can be applied under diverse test conditions with a predetermined period of the operational life of the metallic glasses as functional materials. Furthermore, variations of the energy efficiency of the metallic glasses as a function of the acid concentration and time were produced by fitting the experimental data to a numerical model using a nonlinear regression method. The profiles of the metallic glasses exhibit a less conservative behavior of energy efficiency than the applied analytical criterion.

Keywords: Energy efficiency, Functional Materials, High entropy metallic glasses, Thin film, Conductivity, EIS, Hydrochloric acid.

Introduction
In general, it has been known for sometimes that thin films of metallic glasses have many practical applications owing to their extreme homogeneous and disordered, i.e., high entropy, structures [1]. Numerous studies were conducted to illustrate the improvement of mechanical properties as well as the corrosion resistance of the metallic glasses in comparison to their counterparts, the polycrystalline metallic alloys [2-4]. In fact, the practical role of metallic glasses became more significant with the increase of the thickness of the glasses from a micrometer to a millimeter scale [5-7]. In other words, bulk metallic glasses have gained tremendous attention due to higher strength, larger elastic limit and better corrosion resistivity, compared to their polycrystalline counterparts [8-12]. Also, bulk metallic glasses might be used as a small functional metal part; electronics frames and castings, orthopedic screws, cardiovascular stents, surgical instruments, and microelectromechanical devices [11,12]. Therefore, devices made of bulk metallic glasses require maintenance on a frequent basis, especially when those devices were implemented as integrated assembly parts of machinery/structures. The maintenance is essential due to contaminations of the surrounding environment. Consequently, EIS will be used to measure parameters such as the alternating current impedance and the conductivity of the iron-boron-silicon metallic glasses in hydrochloric acid solutions. The reason for testing in hydrochloric acid solutions is to simulate the surrounding environment of metallic glasses in case the glasses are implemented as integrated assembly parts of machinery/structures. The selection of hydrochloric acid solutions is based on examining the metallic glasses to an extreme scenario case for this investigation. Then, the obtained parameters of the EIS tests will be compared with those of the metallic glasses in the air. As a result, the variation of the energy efficiency of the metallic glasses will be determined in different conditions. The energy efficiency will be calculated based on the variation of the conductivity of the metallic glasses in the air compared to the steady value in aqueous solution. In the present

work, a criterion of the energy efficiency of the metallic glasses was developed. The proposed criterion; lim $(\sigma_s/\sigma_{air}) = 1$ will determine the energy efficiency of the metallic glasses in aqueous solutions when σ_{air} becomes equal (decreases) to the steady value of σ_s as a function of time of the exposure of the material to the aqueous solution. The criterion was plotted based on obtained conductivity values of the metallic glasses in hydrochloric acid solutions by EIS versus the predetermined operation time of the metallic glasses. The conductivity value of the metallic glasses can be measured as follows [13]:

$$\sigma = U/RA = 1/\rho \qquad (1)$$

where,

σ is the electrical conductivity of the metallic glasses, Siemens/cm;

R is the direct current (DC) resistance of the metallic glasses, Ohm;

A is the exposed surface area of the sample to the solution, cm^2;

U is the thickness of the metallic glasses, µm.

ρ is the electrical resistivity of the metallic glasses, Ohm-cm;

Equation (1) can be used to determine the conductivity of metallic glasses samples in aqueous solution by the substitution of the value of alternating current impedance (|Z|, Ohm) in the place of the value of R. This is valid when the |Z| value was measured by the technique of electrochemical impedance spectroscopy (EIS) at very low frequency, at room temperature [14-16]. In other words, Eq. (1) can be rewritten to a modified version of the following form:

$$\sigma = U/\,|Z|A \qquad (2)$$

Therefore, the model of the energy efficiency of the metallic glasses can be derived from Eq. (2) as follows:

$$\lim_{\sigma_{air} \to \sigma_s} (\sigma_s/\,\sigma_{air}) = 1 \qquad (3)$$

where,

σ_s is the invariant conductivity of the metallic glass sample in aqueous solutions, Siemens/cm.

σ_{air}air is the variant conductivity of the metallic glass sample in air, Siemens/cm.

Equation (3) states that when the variant value of σ_{air} becomes equal (decreases) to the invariant value of σ_s as a function of time of the exposure of the sample to the aqueous solution, the sample is no longer energy efficient.

In addition to the analytical work of the derivation of the equation (3), numerical profiles of the energy efficiency of the metallic glasses (σ_s/σ_{air}) as a function of the acid concentration and time were produced by fitting the experimental data to a model using a nonlinear regression method [17]. The model can be given as:

$$\frac{\sigma_s}{\sigma_{air}} = \frac{e^{\frac{\eta+5}{50}t} - e^{-\frac{\eta+5}{50}t}}{e^{\frac{\eta+5}{50}t} + e^{-\frac{\eta+5}{50}t}} \qquad (4)$$

where η is the concentration of the HCl solutions and t is the time of exposure.

The numerical profiles were obtained based on a value range of (σ_s/σ_{air}) between 0–1. Since η is known for the 25–100% HCl solutions, therefore, t can accordingly be determined.

Experimental Works

In this investigation, Eq. (3) was applied to determine the energy efficiency of metallic glasses. The chemical composition of the metallic glasses was $Fe_{78}B_{13}Si_9$, $Fe_{81}B_{13}.5Si_{3.5}C_2$, and $Fe_{66}Co_{18}B_{15}Si_1$ with a thin film thickness of 16.6µm, 23.1µm, and 20µm, respectively. In addition, x-ray diffraction (XRD) patterns of the four glasses were obtained to confirm their amorphous structures. Examples of XRD patterns of the investigated metallic glasses are given elsewhere [18].

EIS measurements were performed against a saturated Calomel electrode (SCE) according to standard procedures described elsewhere [14-16]. A standard electrochemical cell of three electrodes was used. The cell made of a 1000 cm^3 flask, a reference electrode (the SCE), a counter electrode (made of high-density graphite bar) and a working electrode of the metallic glasses. The exposed surface area of all samples was 1.0 cm^2. In this study, EIS measurements were conducted using a potentiostat/Galvanostat made by EG&G Princeton Applied Research (PAR) Model 273A. The potentiostat/Galvanostat comes with lock-in Amplifier Model 5210 to obtain impedance spectra. The EIS spectra of all investigated samples were determined in 25%, 50%, 75%, and 100% hydrochloric acid (HCl) solutions. The EIS spectra were basically the complex plane plots (Nyquist plots) and the Bode plots [14-16]. The complex plane plots (Nyquist plots) are basically the imaginary impedance (Z_{imag}) versus the real impedance (Z_{real}). Also, the values of the AC impedance were obtained from Bode plots at a low frequency for all investigated samples. The AC impedance was obtained at a low frequency based on the extrapolation of the intersection line at a frequency equal to 0.16 Hz from the x-coordinate in Bode plots, to the y-coordinate in Bode plot. Bode plots are basically the logarithm of impedance (Z) (Y-coordinate) and the phase (θ) (Y- coordinate) plotted versus the logarithm of the frequency (X-coordinate). All the AC impedances of the investigated samples were determined by using EG7G based software, using the data fitting method of Randell's semicircle. A frequency range was chosen between 100000 to 0.01 Hz in order to plot the complex plane (Nyquist) and Bode plots. The AC impedance (Z) values of the samples were determined from Bode plots at a frequency is equal to f = 0.16 Hz (at angular velocity ϖ = 1 rad/s), where ϖ =2πf. From Eq. (3), the values of σ_s, σ_{air}, and (σ_s/σ_{air}) were calculated based on the obtained data of |Z| from the EIS tests of the metallic glasses [14-16]. In addition, the value of σ_{air} of the metallic glasses was obtained elsewhere [19] from the values of $\sigma_{air}=1/\rho_{air}$. Figure 1a,b is an example of a Bode plot of the $Fe_{81}B_{13.5}Si_{3.5}C_2$ metallic glass in 25%, 50%, 75%, and 100% HCl solutions [18]. The obtained data of |Z| of the metallic glasses are given in Table I. In addition, the calculated parameters of σ_s (from Eq.2) and (σ_s/σ_{air}) (from Eq.3) are given in Table II and Table III, respectively.

Results and Discussion

In general, the impedance (|Z|) of all investigated metallic glasses tends to decrease with the increase of the concentration of HCl solution, see Table I. However, the $Fe_{78}B_{13}Si_9$ metallic glass was recorded to have the lowest value of |Z| among all investigated glasses in 25% HCl solution. In contrast, the $Fe_{78}B_{13}Si_9$ metallic glass was recorded to have the highest value of |Z| among all investigated glasses in 100% HCl solution. The |Z| value of the $Fe_{78}B_{13}Si_9$ metallic glass was found to correspond well with the calculated value of the conductivity of the same glass in 25% & 100% & HCl solutions, as shown in Table II. In other words, the conductivity value decreases with the increase of the |Z| value, in an inversely proportional manner. In the meantime, the energy efficiency $(\sigma_s/\,\sigma_{air})$ of all tested glasses was observed to increase as a function of HCl concentration. The highest value of ($\sigma_s/\ \sigma_{air}$= 2.3x$10^{-8.5}$) was found for $Fe_{78}B_{13}Si_9$ in 100% HCl. In contrast, the lowest value of ($\sigma_s/\ \sigma_{air}$= 2.3x$10^{-10.0}$) was found for $Fe_{78}B_{13}Si_9$ in 25% HCl, see Table III.

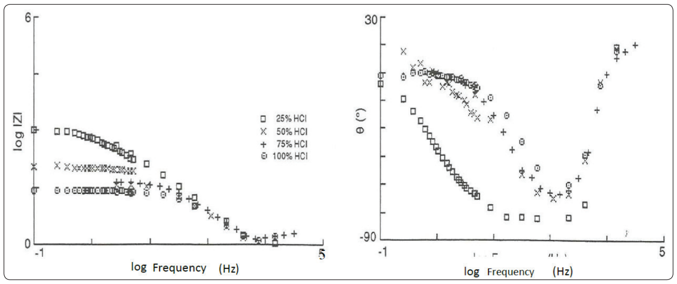

Figure 1: a,b Bode plot of $Fe_{78}B_{13}Si_9$ sample in 25%, 50%, 75%, and 100% HCl solutions. Fig.1a is the logarithm of impedance (Z) versus the logarithm of frequency and Fig.1b is the phase angle (θ) versus the logarithm of the frequency.

Table I: The obtained data of |Z| of the metallic glasses in 25%, 50%, 75%, and 100% HCl solutions

(A.C. Impedance (Ohm))			
Solutions	**$Fe_{78}B_{13}Si_9$**	**$Fe_{81}B_{13.5}Si_{3.5}C_2$**	**$Fe_{66}Co_{18}B_{15}Si_1$**
25% HCl	$10^{3.0}$	$10^{2.7}$	$10^{2.9}$
50% HCl	$10^{2.0}$	$10^{2.0}$	$10^{2.6}$
75% HCl	$10^{1.8}$	$10^{2.7}$	$10^{2.9}$
100% HCl	$10^{1.5}$	$10^{1.7}$	$10^{1.7}$

TABLE II. Calculated parameters of σ_s (from Eq.2) of the metallic glasses in 25%, 50%, 75%, and 100% HCl solutions

(Conductivity (Siemen/cm))			
Solutions	**$Fe_{78}B_{13}Si_9$**	**$Fe_{81}B_{13.5}Si_{3.5}C_2$**	**$Fe_{66}Co_{18}B_{15}Si_1$**
0% HCl (In air) [19]	7.3x10^3	7.4x10^3	8.1x10^3
25% HCl	16.7x$10^{-7.0}$	23.1x$10^{-6.7}$	20x$10^{-6.9}$
50% HCl	16.7x$10^{-6.0}$	23.1x$10^{-6.0}$	20x$10^{-6.6}$
75% HCl	16.7x$10^{-5.8}$	23.1x$10^{-6.7}$	20x$10^{-6.9}$
100% HCl	16.7x$10^{-5.5}$	23.1x$10^{-5.7}$	20x$10^{-5.7}$

TABLE III. The calculated parameters of ($\sigma_s/\ \sigma_{air}$) (from Eq.3) of the metallic glasses in 25%, 50%, 75%, and 100% HCl solutions

($\sigma_s/\ \sigma_{air}$)			
Solutions	**$Fe_{78}B_{13}Si_9$**	**$Fe_{81}B_{13.5}Si_{3.5}C_2$**	**$Fe_{66}Co_{18}B_{15}Si_1$**
0% HCl (In air) [19]	1.0	1.0	1.0
25% HCl	2.3x$10^{-10.0}$	3.1x$10^{-9.7}$	2.5x$10^{-9.9}$
50% HCl	2.3x$10^{-9.0}$	3.1x$10^{-9.0}$	2.5x$10^{-9.6}$
75% HCl	2.3x$10^{-8.8}$	3.1x$10^{-9.7}$	2.5x$10^{-9.9}$
100% HCl	2.3x$10^{-8.5}$	3.1x$10^{-8.7}$	2.5x$10^{-8.7}$

Figures 2 and 3 illustrate the lim ($\sigma_s/\ \sigma_{air}$) versus time of exposure for energy efficiency of the $Fe_{78}B_{13}Si_9$ samples in 25% HCl and 100% HCL, respectively. Figs.2 and 3 were plotted at time of exposure=0, at which the values of ($\sigma_s/\ \sigma_{air}$) = 2.3x$10^{-10.0}$ and ($\sigma_s/\ \sigma_{air}$)=2.3x$10^{-8.5}$ for the $Fe_{78}B_{13}Si_9$ samples in 25% HCl and 100% HCl, were nearly equal zero, respectively. Furthermore, at time of exposure=24 months, Figs.2 and 3 were plotted; ($\sigma_s/\ \sigma_{air}$)=($\sigma_s/\ \sigma_{air}$) = 1, and ($\sigma_s/\ \sigma_{air}$)= ($\sigma_s/\ \sigma_{air}$) = 1 for the $Fe_{78}B_{13}Si_9$ samples in 25% HCl and 100% HCl, respectively, assuming the operational time will last 24 months.

Figs. 2 and 3 show two regions. One region is below the line in the Figs, in which the metallic glasses is energy efficient enough with respect to the proposed criterion of Eq.(3). The other region is above the line in the Figs, in which the material is not energy efficient with respect to the proposed criterion of Eq.(3). In this case, maintenance (cleaning) or a replacement of the material is essential for better efficiency. The energy efficiency of the material can be actually determined by measuring σ_s , σ_{air} , and then calculating the lim ($\sigma_s/\ \sigma_{air}$) on a frequent basis during a predetermined time of the material's operation. Then, the obtained value of lim ($\sigma_s/\ \sigma_{air}$) can be compared with a standard plot of lim ($\sigma_s/\ \sigma_{air}$) like those in Figs.2 and 3 with a specific time of operation. So, Figs.2 and 3 can be standard plots of energy efficiency for different kinds of functional materials.

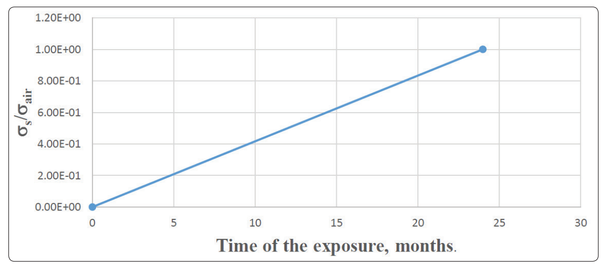

Figure 2: lim (σ_s/σ_{air}) versus Time of exposure for energy efficiency of the $Fe_{78}B_{13}Si_9$ samples in 25% HCl

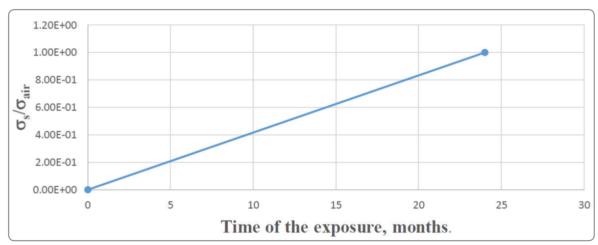

Figure 3: lim (σ_s/σ_{air}) versus Time of exposure for energy efficiency of the $Fe_{78}B_{13}Si_9$ samples in 100% HCl

Along with the conservative approach of determining the energy efficiency, equation (3), of metallic glasses in acid solutions, a practical approach was derived by fitting the experimental data to a mathematical model equation (4) using a nonlinear regression method [17]. Figure 4 illustrates an example of numerical profiles of the energy efficiency, equation (4) of the $Fe_{78}B_{13}Si_9$ samples as a function of time and HCl concentration, in comparison to the applied criterion of equation (3).

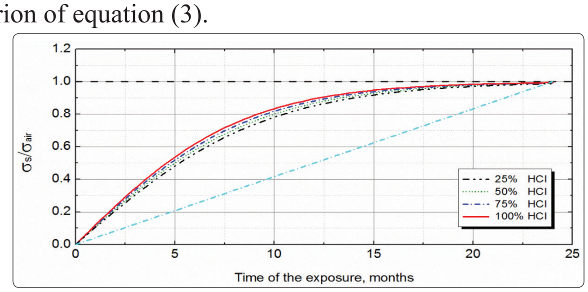

Figure 4: lim (σ_s/σ_{air}) versus Time of exposure for energy efficiency of the $Fe_{78}B_{13}Si_9$ samples in 25%, 50%, 75%, and 100% HCl

It is obvious from figure 4 that the numerical profiles of the energy efficiency, equation (4) are more practical than the applied criterion, equation (3), of the metallic glasses. In other words, the energy efficient region, below the line/profiles, increases with increasing the HCl concentration.

Conclusion Remarks

A developed criterion of the energy efficiency of metallic glasses was implemented on Fe-B-Si metallic glasses in HCl solutions. The criterion was derived based on calculating the limit of the ratio value of the conductivity of a metallic glass in aqueous solution (σ_s) to the conductivity of the metallic glass material in air (σ_s / σ_{air}) Plots of the lim (σ_s / σ_{air}) versus time of exposure were obtained for energy efficiency of the pure $Fe_{78}B_{13}Si_9$ samples in 25% HCl and 100% HCl. Therefore, plots of the lim (σ_s / σ_{air}) versus Time of exposure like those of Figs.2 and 3 can be standard plots of the energy efficiency for different kinds of functional materials. In addition, numerical profiles of the energy efficiency of the metallic glasses as a function of the acid concentration and time were produced by fitting the experimental data to a model using a nonlinear regression method. The numerical profiles of the energy efficiency, equation (4) were found more practical than the applied criterion, equation (3), of the metallic glasses.

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