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Energy Efficiency of Iron-Boron-Silicon Metallic Glasses in Sulfuric Acid Solutions

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Abstract
A criterion of the energy efficiency of iron-boron-silicon metallic glasses in sulfuric acid solutions is proposed for the first time. The criterion has been derived based on calculating the limit of the ratio value of the conductivity of a metallic glass in aqueous solution to the conductivity of the metallic glass in air. In other words, the conductivity ratio of a 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 not only used to determine the energy efficiency of different metallic glasses, but also, the criterion was used to determine the energy efficiency of metallic glasses exposed to a wide range of sulfuric acid concentrations. These conductivity values 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 the energy efficiency than the proposed analytical criterion.

Keywords: Energy efficiency; Metallic glasses; Conductivity; Electrochemical impedance spectroscopy; Sulfuric acid; and Electrical power consumption.
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 structures \[^{[1]}\]. Many studies were conducted to demonstrate the improvement of mechanical properties as well as the corrosion resistance of the metallic glasses in a 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 considerable attention due to higher strength, larger elastic limit and better corrosion resistivity, compared to their polycrystalline counterparts \[^{[8-11]}\]. Besides these, bulk metallic glasses can also be used as a small functional metal parts; electronics frames and castings, orthopedic screws, cardiovascular stents, surgical instruments, and microelectromechanical devices \[^{[11]}\]. Therefore, devices made of bulk metallic glasses require a more frequent maintenance, especially when those devices implemented as integrated assembly parts of machineries or structures. Maintenance of the metallic glass surface is essential due to contaminations from 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 sulfuric acid solutions. The reason of testing in the sulfuric acid solutions is to simulate exposure to the corrosive surrounding or the environment of metallic glasses in case the glasses are implemented as integrated assembly parts of machineries or structures. The selection of sulfuric acid solutions is based on examining the metallic glasses to an extreme scenario case for this investigation. Subsequently, the obtained parameters for the EIS tests will be compared with those of the metallic glasses in 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 air compared to the constant value in the acid solution. In the present work, a criterion of the energy efficiency of the metallic glasses is developed. The proposed criterion; \( \lim (\sigma_s/\sigma_{\text{air}}) =1 \) will determine the energy efficiency of the metallic glasses in aqueous solutions when \( \sigma_{\text{air}} \) becomes equal (decreases) to the steady value of \( \sigma_s \) as a function of time of the exposure of the material to the aqueous solution. The criterion was plotted based on
conductivity values obtained for the metallic glasses in sulfuric acid solutions by EIS versus the predetermined operational time of the metallic glasses. The conductivity value of the metallic glasses can be measured as follows [12]:

$$\sigma = \frac{U}{RA} = \frac{1}{\rho}$$  

(1)

where,

- \(\sigma\) is the electrical conductivity of the metallic glasses, Siemen/cm;
- \(R\) is the direct current (DC) resistance of the metallic glasses, Ohm;
- \(A\) is the exposed surface area of the sample to solution, cm\(^2\);
- \(U\) is the thickness of the metallic glasses, \(\mu\)m.
- \(\rho\) 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 substituting 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 electrochemical impedance spectroscopy (EIS) technique at a very low frequency, at the room temperature [13-15]. In other words, Eq. (1) can be rewritten to a modified version of the following form:

$$\sigma \quad = \quad \frac{U}{|Z|A}$$

(2)

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

$$\lim \left( \frac{\sigma_s}{\sigma_{air}} \right) = 1$$

(3)

where,

- \(\sigma_s\) is the invariant conductivity of the metallic glass sample in aqueous solutions, Siemen/cm.
- \(\sigma_{air}\) is the variant conductivity of the metallic glass sample in air, Siemen/cm.

Equation (3) states that when the variant value of \(\sigma_{air}\) becomes equal (decreases) to the invariant value of \(\sigma_s\) as a function of time of the exposure of the sample to the aqueous solution, the
The electrical power consumption of the metallic glasses in terms of the electrical current (I) and $\sigma$ can be derived as follows:

$$P=I^2R = I^2U/(\sigma A)$$  \hspace{1cm} (4)

The electrical power consumption will increase inversely with the decrease of the $\sigma_{\text{air}}$ to the value of $\sigma_s$ as a function of exposure time of the sample to the aqueous solution. In a similar manner to the derivation of Eq.(3), the following relationship can be derived:

$$\lim \left( \frac{P_{\text{air}}}{P_s} \right) = 1$$  \hspace{1cm} (5)

where,

$P_s$ is the invariant electrical power consumption of the metallic glass sample in aqueous solutions, Watt.

$P_{\text{air}}$ is the variant electrical power consumption of the metallic glass sample in air, Watt.

Equation (5) states that when the variant value of $P_{\text{air}}$ becomes equal (increases) to the invariant value of $P_s$ 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 Eq.(3), numerical profiles of the energy efficiency of the metallic glasses ($\sigma_s/\sigma_{\text{air}}$) as a function of the acid concentration and time were produced by fitting the experimental data to a model using a nonlinear regression method\textsuperscript{16}.

The model can be given as:

$$\frac{\sigma_s}{\sigma_{\text{air}}} = \frac{e^{\frac{4\eta+3}{40}t} - e^{-\frac{4\eta+3}{40}t}}{e^{\frac{4\eta+3}{40}t} + e^{-\frac{4\eta+3}{40}t}}$$  \hspace{1cm} (6)

where,

$\eta$ is the concentration of the H$_2$SO$_4$ solutions.

$t$ is the time of exposure, month.

The numerical profiles were obtained based on a value range of ($\sigma_s/\sigma_{\text{air}}$) between 0-1. Since, $\eta$ is known for the 25-100% H$_2$SO$_4$ solutions, therefore, $t$ can accordingly be determined.

Finally, the experimental data of the proposed criterion of the energy efficiency will be compared to the numerical profiles of the metallic glasses.

**Experimental Works**
In this investigation, Eq. (3) was used for the first time to determine the energy efficiency of metallic glasses. The chemical composition of the metallic glasses were Fe$_{78}$B$_{13.5}$Si$_{9}$, Fe$_{81}$B$_{13.5}$Si$_{3.5}$C$_{2}$, and Fe$_{66}$Co$_{18}$B$_{15}$Si$_{1}$ with a thin film thickness of 16.6 µm, 23.1µm, and 20 µm, respectively. EIS measurements were performed against a saturated Calomel electrode (SCE) according to standard procedures described elsewhere [13-15]. A standard electrochemical cell with 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 in order to obtain impedance spectra. The EIS spectra of all investigated samples were determined in 25%, 50%, 75%, and 100% sulfuric acid (H$_2$SO$_4$) solutions. The EIS spectra [13-15] were basically the complex plane plots (Nyquist plots) and the Bode plots. The complex plane plots (Nyquist plots) are basically the imaginary impedance ($Z_{\text{imag}}$) versus the real impedance ($Z_{\text{real}}$). The AC impedance values were also obtained from the Bode plots at a low frequency for all investigated samples. The AC impedances were obtained at 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 ($\theta$) (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 the Randell’s semicircle. Also, in order to plot the complex plane (Nyquist) and Bode plots, the frequency range was chosen to be between 100000 to 0.01 Hz. The AC impedance ($Z$) values of the samples were determined from Bode plots [13-15] at a frequency is equal to $f = 0.16$ Hz (at angular velocity $\omega = 1$ rad/s), where $\omega = 2\pi f$. From Eq.(3), the values of $\sigma_s$, $\sigma_{\text{air}}$, and ($\sigma_s/\sigma_{\text{air}}$) were calculated based on the obtained data of $|Z|$ from the EIS tests of the metallic glasses. In addition, values of $\sigma_{\text{air}}$ of the metallic glasses were obtained elsewhere [2] from the values of $\rho_{\text{air}}$=1/$\sigma_{\text{air}}$. Figure 1 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% H$_2$SO$_4$ solutions. The obtained data of $|Z|$ of the metallic glasses are given in Table I. In addition, the calculated parameters of $\sigma_s$ (from Eq.2) and ($\sigma_s/\sigma_{\text{air}}$) (from Eq.3) are
given in Tables II and III, respectively. Furthermore, the calculated parameters of \( \frac{P_{\text{air}}}{P_s} \) (from Eq.5) of the metallic glasses in 25\%, 50\%, 75\%, and 100\% H\textsubscript{2}SO\textsubscript{4} solutions are given in Table IV.

**Results and Discussion**

In general, the impedance (|\( Z \)|) of all investigated metallic glasses tends to increase with the increase in the concentration of H\textsubscript{2}SO\textsubscript{4} solution, as shown in Table I. However, the Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} metallic glass was recorded to have the lowest value of |\( Z \)| among all investigated glasses in 25\% H\textsubscript{2}SO\textsubscript{4} solution. In contrast, the Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} metallic glass was recorded to have the highest value of |\( Z \)| among all investigated glasses in 100\% H\textsubscript{2}SO\textsubscript{4} solution. The |\( Z \)| value of the Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} metallic glass was found to correspond well with the calculated value of the conductivity of the same glass in 25\% & 100\% & H\textsubscript{2}SO\textsubscript{4} solutions, see 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 (\( \sigma_s/\sigma_{\text{air}} \)) of all tested glasses was recorded to decrease as a function of H\textsubscript{2}SO\textsubscript{4} concentration, see Table III. The highest value of (\( \sigma_s/\sigma_{\text{air}}=16.7\times10^{-4.25} \)) was found for Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} in 25\%H\textsubscript{2}SO\textsubscript{4}. In contrast, the lowest value of (\( \sigma_s/\sigma_{\text{air}}=2.3\times10^{-10.25} \)) was found for Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} in 100\%H\textsubscript{2}SO\textsubscript{4}. On the contrary, The electrical power consumption (\( P_{\text{air}}/P_s \)) of the metallic glasses was recorded to increase as a function of H\textsubscript{2}SO\textsubscript{4} concentration, see Table IV. A range of the lowest and highest values was found between \( P_{\text{air}}/P_s = 0.43\times10^{-7.25} \) and \( P_{\text{air}}/P_s = 0.43\times10^{10.25} \) for Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} in 25\%H\textsubscript{2}SO\textsubscript{4} and Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} in 100\%H\textsubscript{2}SO\textsubscript{4}, respectively. The behavior of the electrical power consumption (\( P_{\text{air}}/P_s \)) is in a good agreement with the obtained data of the energy efficiency (\( \sigma_s/\sigma_{\text{air}} \)) of metallic glasses in H\textsubscript{2}SO\textsubscript{4} solutions.
Fig. 1 Bode plot of Fe$_{81}$B$_{13.5}$Si$_{3.5}$C$_2$ sample in 25%, 50%, 75%, and 100% H$_2$SO$_4$ 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% H$_2$SO$_4$ 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% H$_2$SO$_4$                 | $10^{0.25}$             | 10                          | $10^{1.25}$                     |
| 50% H$_2$SO$_4$                 | $10^{2.5}$              | $10^{2.25}$                 | $10^{1.8}$                      |
| 75% H$_2$SO$_4$                 | $10^{1.5}$              | $10^{1.4}$                  | $10^{2.3}$                      |
| 100% H$_2$SO$_4$                | $10^{3.25}$             | $10^{1.4}$                  | $10^{2.3}$                      |

<table>
<thead>
<tr>
<th>TABLE II. Calculated parameters of σ$_s$ (from Eq.2) of the metallic glasses in 25%, 50%, 75%, and 100% H$_2$SO$_4$ solutions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Conductivity (Siemen/cm))</td>
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<tr>
<td>Solutions</td>
</tr>
<tr>
<td>25% H$_2$SO$_4$</td>
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<tr>
<td>50% H$_2$SO$_4$</td>
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<tr>
<td>75% H$_2$SO$_4$</td>
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<tr>
<td>100% H$_2$SO$_4$</td>
</tr>
</tbody>
</table>
0% H₂SO₄ (In air)[²] & 7.3x10³ & 7.4x10³ & 8.1x10³ \\
25% H₂SO₄ & 16.7x10⁻⁸.₂⁵ & 23.1x10⁻⁵ & 20x10⁻⁵.₂⁵ \\
50% H₂SO₄ & 16.7x10⁻⁶.₅ & 23.1x10⁻⁵.₂⁵ & 20x10⁻⁵.₈ \\
75% H₂SO₄ & 16.7x10⁻⁵.₅ & 23.1x10⁻⁵.₄ & 20x10⁻⁵ \text{.}₃ \\
100% H₂SO₄ & 16.7x10⁻⁷.₂⁵ & 23.1x10⁻⁵.₄ & 20x10⁻⁶.₃ \\

TABLE III. The calculated parameters of \((\sigma_s/\sigma_{\text{air}})\) (from Eq.3) of the metallic glasses in 25%, 50%, 75%, and 100% H₂SO₄ solutions.

\[
\begin{array}{ccc}
\text{Solutions} & \text{Fe₇₈B₁₃Si₉} & \text{Fe₈₁B₁₃.₅Si₉.₅C₂} & \text{Fe₆₆Co₁₉B₁₂Si₄} \\
0% \text{ H₂SO₄} & 1.0 & 1.0 & 1.0 \\
25% \text{ H₂SO₄} & 2.3x10⁻⁷.₂⁵ & 3.1x10⁻⁸ & 2.5x10⁻⁸.₂⁵ \\
50% \text{ H₂SO₄} & 2.3x10⁻⁹.₅ & 3.1x10⁻⁸.₂⁵ & 2.5x10⁻⁸.₈ \\
75% \text{ H₂SO₄} & 2.3x10⁻⁹.₅ & 3.1x10⁻⁸.₄ & 2.5x10⁻⁹.₃ \\
100% \text{ H₂SO₄} & 2.3x10⁻¹⁰.₂⁵ & 3.1x10⁻⁸.₄ & 2.5x10⁻⁹.₃ \\
\end{array}
\]

Figures 2 and 3 illustrate the lim \((\sigma_s/\sigma_{\text{air}})\) versus time of exposure for energy efficiency of the Fe₇₈B₁₃Si₉ samples in 25% H₂SO₄ and 100% H₂SO₄, respectively. Figures 2 and 3 were plotted at a time of exposure=0, at which the values of \((\sigma_s/\sigma_{\text{air}}) = 16.7x10⁻⁴.₂⁵ \) and \((\sigma_s/\sigma_{\text{air}}) = 2.3x10⁻¹⁰.₂⁵ \) for the Fe₇₈B₁₃Si₉ samples in 25%H₂SO₄ and 100%H₂SO₄, were nearly equal zero, respectively.
Furthermore, at time of exposure=24 months, Figs.2 and 3 were plotted; \( \left( \sigma_s/\sigma_{\text{air}} \right) = \sigma_s=\sigma_{\text{air}} = 1 \), and \( ( \sigma_s/\sigma_{\text{air}} ) = \sigma_s=\sigma_{\text{air}} = 1 \) for the Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} samples in 25\% H\textsubscript{2}SO\textsubscript{4} and 100\% H\textsubscript{2}SO\textsubscript{4}, respectively, assuming the operational time will last 24 months.

Figures 2 and 3 show two regions. One region is below the blue line, in which the metallic glasses is energy efficient enough with respect to the proposed criterion of Eq.(3). The other region is above the blue line, in which the material is not energy efficient with respect to the proposed criterion of Eq.(3). In this case, a 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 \( \sigma_s, \sigma_{\text{air}} \), and then calculating \( \lim \left( \sigma_s/\sigma_{\text{air}} \right) \) on a frequent basis, i.e., once a month, during a predetermined time of the material’s operation. Then, the obtained value of \( \lim \left( \sigma_s/\sigma_{\text{air}} \right) \) can be compared with a standard plot of \( \lim \left( \sigma_s/\sigma_{\text{air}} \right) \) 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.

![Graph](image)

Fig.2. \( \lim \left( \sigma_s/\sigma_{\text{air}} \right) \) versus Time of exposure for energy efficiency the for the Fe\textsubscript{78}B\textsubscript{13}Si\textsubscript{9} samples in 25\% H\textsubscript{2}SO\textsubscript{4}. 
Fig. 3. lim (σ_s/σ_{air}) versus Time of exposure for energy efficiency for the Fe_{78}B_{13}Si_{9} samples in 100% H_{2}SO_{4}.

Along with the conservative approach of determining the energy efficiency, Eq.(3), of metallic glasses in acid solutions, a practical approach was derived by fitting the experimental data to a mathematical model Eq.(6) using a nonlinear regression method^{16}. Figure 4 illustrates an example of numerical profiles of the energy efficiency, Eq.(6) of the Fe_{78}B_{13}Si_{9} samples as a function of time & H_{2}SO_{4} concentration, in a comparison to the proposed criterion of Eq.(3)
Fig. 4 lim ($\sigma_s/\sigma_{air}$) versus Time of exposure for energy efficiency for the Fe$_{78}$B$_{13}$Si$_9$ samples in 25%, 50%, 75% and 100% H$_2$SO$_4$.

It is quite obvious from Fig.4 that the numerical profiles of the energy efficiency, Eq.(6) are more practical than the proposed criterion , Eq.(3), of the metallic glasses. In other words, the energy efficient region, below the line/profiles, increases with increasing the H$_2$SO$_4$ concentration.

**Concluding Remarks**

A criterion of the energy efficiency of metallic glasses was developed. The criterion was derived based on calculating the ratio of the conductivity values of a metallic glass in aqueous solution ($\sigma_s$) to the conductivity of the metallic glass material in air ($\sigma_{air}$). Plots of the lim ($\sigma_s/\sigma_{air}$) versus time of exposure were obtained for energy efficiency of the pure Fe$_{78}$B$_{13}$Si$_9$ samples in 25% H$_2$SO$_4$ and 100% H$_2$SO$_4$. Consequently, two regions were defined in the plots of the lim ($\sigma_s/\sigma_{air}$) versus time. 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, a maintenance (cleaning) or a replacement of the material is essential for better efficiency. Therefore, plots of the lim ($\sigma_s/\sigma_{air}$) 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, Eq.(6) were found more practical than the proposed criterion , Eq.(3), of the metallic glasses.

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