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MODIFIED ELECTROCHEMICAL EMISSION SPECTROSCOPY(MEES) AS NDT METHOD OF DETECTION OF SCC OF METALLIC GLASSES

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ABSTRACT

A preliminary study on the susceptibility of various iron-boron-silicon metallic glasses to stress-corrosion cracking (SCC) has been conducted. Testing was carried out on thin metallic ribbons of $Fe_{78}B_{13}Si_{9}$, $Fe_{81}B_{13.5}Si_{3.5}C_{2}$, $Fe_{66}Co_{18}B_{15}Si_{1}$, $Fe_{77}B_{16}Cr_{2}Si_{5}$, and $Fe_{40}Ni_{38}Mo_{4}B_{18}$, in 0%, 25%, 50%, 75%, and 100% hydrochloric acid solutions at the open circuit potential of the metallic glasses in solutions, at room temperature. The tests were performed under constant-strain conditions in the various solutions until complete separation of the ribbons occurred. The preliminary results indicated that the susceptibility of the glasses $Fe_{78}B_{13}Si_{9}$, $Fe_{81}B_{13.5}Si_{3.5}C_{2}$, $Fe_{66}Co_{18}B_{15}Si_{1}$, and $Fe_{77}B_{16}Cr_{2}Si_{5}$, to stress-corrosion cracking varies only as a function of the amplitude of the strain. The susceptibility to SCC is independent of the solution concentration and the addition of carbon, chromium, and cobalt to the glass. However, the results indicated that $Fe_{40}Ni_{38}Mo_{4}B_{18}$ glass is not susceptible to stress-corrosion cracking in HCl solutions at different strain amplitudes.

In addition, an early stage of stress corrosion cracking (SCC) of the same metallic glasses in the same solutions was investigated in situ by a new non-destructive testing (NDT) method. The new method of SCC detection is based on the optical corrosion-meter for measuring the corrosion current density (J) and on a modified electrochemical noise technique for determining the corrosion admittance (Ac) at the open circuit potential of the alloys in solutions, at room temperature. A comparison between the two techniques of SCC study indicates that the new method has many advantages relatives to the constant-strain method.

KEYWORDS : Stress Corrosion Cracking (SCC), Metallic Glass, Electrochemical Noise, Constant Strain, Non-Destructive Method, Corrosion Admittance, Holographic interferometry , and HCl Solution.

INTRODUCTION

It has been known for some time that thin films of metallic glasses have many practical values owing to their extremely homogeneous and disordered atomic structures [1]. For instance, Allied Chemical Inc., has recently reported results on a $Fe_{78}B_{13}Si_{9}$ metallic thin film, known commercially as Metglass 2605S [2], indicating that the film has excellent physical and magnetic properties as compared to the crystalline alloy. The film was found suitable for extremely low core loss in distribution, power transformers, and motors. It combines high induction and superb magnetic properties at frequencies, induction, and operating temperatures of these devices. Furthermore, the film can be used in inductors, current transformers and other devices requiring high permeability and low core loss at low frequencies.

Subsequently, Allied Chemical succeeded in developing three new metallic films ($Fe_{81}B_{13.5}Si_{3.5}C_2$ known as Metglas 2605SC, $Fe_{66}Co_{18}B_{15}Si_1$ known as Metglas 2605Co, and $Fe_{77}Cr_2B_{16}Si_5$ known as Metglas 2605 S3-A) with improved physical and magnetic properties. Detailed information on these films has been well documented elsewhere [3]. In addition to the Fe-B-Si glasses, an Fe-Ni glass, $Fe_{40}Ni_{38}Mo_4B_{18}$ known as Metglas 2826 MB, was among the first Metglas alloys developed by Allied Chemical. The $Fe_{40}Ni_{38}Mo_4B_{18}$ glass has a high content of corrosion resistant elements (Ni and Mo) in a comparison with the other glasses. Information on the internal structures and properties of the Fe_{40} Ni_{38} Mo_4 B_{18}, are reported elsewhere [4 & 5].

Specifically, the properties of the Fe_{81} $B_{13.5}$ $Si_{3.5}$ C_2, are balanced in a way that may lend the films useful in pulse transformers, magnetic amplifiers, power transformers, current transducers and other devices requiring a square-loop high saturation material. The film also offers a unique combination of high resistivity, high saturation induction, and very low core loss, making it suitable for use from low to high frequencies. Fe_{66} Co_{18} B_{15} Si_1 exhibits the highest saturation induction of any amorphous alloy commercially available. In addition, it possesses very low core loss and it is designed ideally for pulse applications where maximum flux swing is desired. However, Fe_{77} Cr_2 B_{16} Si_5 is found to exhibit very low core loss at high frequencies (>1 KHz) when annealed to obtain a rounded B-H Loop. Its saturation induction is much higher than ferrites and can be used at elevated temperatures without cracking or showing large drops in usable flux density. In torodial losses are reduced as temperature increases.

In general, the properties of Fe_{77} Cr_2 B_{16} Si_5 can be substantially tailored by annealing treatment. In addition, the alloy offers an improved high frequency annealing cycle which makes field annealing optional. High frequency losses can be lowered without use of a field while field annealing will increase permeability. Other anneals for low frequencies yield exceptionally high (60 Hz) permeabilities which are useful in current transformers or ground fault protection devices.

On the other hand, the $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy has medium saturation induction. Also, it has lower magnetostriction and higher corrosion resistance than the Fe-B-Si alloys [4 & 5]. The alloy can be annealed for very high DC permeability, and use of the alloy in field sensors and shielding applications is possible. Furthermore, magnetic properties of the alloy can be altered through selective field annealing. Finally, applications for the alloy in manufacturing devices requiring rounded or square B-H Loops are suggested.

In the present investigation, $Fe_{78}B_{13}Si_9$, $Fe_{81}B_{13.5}Si_{3.5}C_2$, $Fe_{66}Co_{18}B_{15}Si_1$ and $Fe_{77}B_{16}Cr_2Si_5$,a$Fe_{40}Ni_{38}Mo_4B_{18}$ glasses were examined for their practical applications as electronic materials [6-8], to the susceptibility of the alloys to stress-corrosion cracking in HCl solutions under a bending stress test [9] and a new non-destructive testing (NDT) method. The new method of SCC detection is based on the optical corrosion-meter [10-20] for measuring the corrosion current density (J) and on a modified electrochemical noise technique for determining the corrosion admittance (Ac) [21-22] at the open circuit potential of the alloys in solutions. The observations of SCC were basically interferometric perturbations detected by the optical corrosion-meter. The interferometric perturbations interpreted as a combined action of a deformation and an electrochemical attack, localized corrosion, in a form of an early stage of SCC, of a deformation ranged between 0.3 μm to several micrometers, of the metallic glasses. Also, the early stage of localized corrosion, i.e., corrosion current corresponding to the deformation, of the same metallic glasses in same conditions was determined in situ by a modified electrochemical noise (EN) technique, called the modified electrochemical emission spectroscopy (MEES) technique, simultaneously during the optical interferometry measurements of the SCC. Determinations of localized corrosion by the MEES technique were electrochemical noise spectra detected on corrosion admittance (Ac)-time plots of the metallic glasses in solutions. The corrosion admittance parameter, Ac=(dJ/dV), which defined the MEES technique, is capable of indicating localized corrosion, as a result of SCC, and uniform corrosion activities. In this investigation, the parameter Ac was modified in which that the change of the corrosion current density (dJ) was measured by the optical corrosion-meter rather than by the zero resistance ammeter,which is usually used for measuring the dJ in electrochemical noise technique.

The modified form is defined as follows:

$$Ac = dJ_o/dV \qquad (1)$$

Where, dJ_o is the difference between the corrosion current density (J) of two subsequent values, and measured by the optical corrosion-meter [18], an electromagnetic method.

dV is the difference between the open circuit potential (V) of two subsequent values [21- 22], normally measured by a potentiometer , an electronic method.

According to (Equ.1), It is generally accepted that the break down passive film (initiation of SCC) will cause a potential drop and a current rise at the same time, and the repassivation of passive film (repassivation of SCC) will cause the potential to increase and the current to decrease. Therefore the Ac parameter , is defined as follows to reflect SCC, passivation or repassivation, and uniform corrosion:

If $A_c < 0$, this indicates that the working electrode under SCC.
If $A_c > 0$, this indicates that the working electrode under uniform corrosion.
If $A_c = 0$, this indicates that the working electrode under passivation or repassivation.

In this way all the corrosion activities (either SCC or uniform corrosion) are clearly revealed in the Ac spectra. Consequently, results of the present work indicate that the optical corrosion-meter as an electromagnetic method of measuring the SCC , and MEES technique, as an electronic method for determining the Ac, are very useful techniques as non-destructive methods for detection of SCC of metallic glasses at the initiation stage of the phenomenon .

EXPERIMENTAL DETAILS

For the bending stress test [9], corrosion samples were prepared from thin foils of the $Fe_{78}B_{13}Si_9$, $Fe_{81}B_{13.5}Si_{3.5}C_2$, $Fe_{66}Co_{18}B_{15}Si_1$, $Fe_{77}Cr_2B_{16}Si_5$, and $Fe_{40}Ni_{38}Mo_4B_{18}$ glasses in a rectangular shape. The length of each sample was approximately 25 mm. The width of the samples varied from one sample to another based on the amplitude of the bending strain during the application of stress to each sample. The thickness of the foils was approximately 16.7 µm for $Fe_{78}B13Si9$, 23.1 µm for $Fe_{81}B_{13.5}Si_{3.5}C_2$, 20 µm for $Fe_{66}Co_{18}B_{15}Si_1$, 16.7 µm for $Fe_{77}Cr_2B_{16}Si_5$, and 16.7 µm for $Fe_{40}Ni_{38}Mo_4B_{18}$ glasses.

The samples were tested as-received and not subjected to any prior heat treatment because of the difficulty in retaining ductility [3]. Stress corrosion tests were conducted in HCl solutions with concentrations in the range of 0-100% HCl until the samples failed. The ribbon samples were bent inside glass tubes of different sizes with each tube size corresponding to a different bending strain (see fig.1). The procedures for calculating the bending strain was based on the following formula [10]:

$$\Sigma = \frac{h/2}{r} \qquad (2)$$

where h stands for the thickness of the ribbon , and r is the internal radius of the glass tube.

It should be noted that because of the thickness of the samples used in the present work, failure criterion was the complete separation of the glasses into two pieces. In the case of the MEES technique for detecting the susceptibility of SCC of the metallic glasses, experimental details will be given in the presentation.

RESULTS AND DISCUSSION

In the case of the bending stress test, the results indicated that $Fe_{78}B_{13}Si_9$, $Fe_{81}B_{13.5}Si_{3.5}C_2$, $Fe_{66}Co_{18}B_{15}Si_1$, and $Fe_{77}Cr_2B_{16}Si_5$ glasses were found susceptible to stress-corrosion cracking in HCl solutions. Samples of the same alloys tested in 0% HCl (distilled water) suffered only from general corrosion attack, rust, during the stress-corrosion tests. Data on strain amplitudes versus time to failure of the different alloys in 25%, 50%, 75% and 100% HCl are presented in tables 1-4. In general, results indicate that the higher the strain, the shorter the life of the samples. All of the samples failed within five hours of immersion in the HCl solutions regardless of the different concentrations of HCl and the additions of the alloying elements (C, Co, Cr) to the Fe-B-Si glass. Consequently, it can be concluded that $Fe_{78}B_{13}Si_9$, $Fe_{81}B_{13.5}Si_{3.5}C_2$, $Fe_{66}Co_{18}B_{15}Si_1$, and $Fe_{77}B_{16}Cr_2Si_5$ glasses have low stress corrosion resistance in HCl solutions.

In addition, results indicated that $Fe_{40}Ni_{38}Mo_4B_{18}$ glass is not susceptible to stress-corrosion cracking in any of the HCl solutions. The alloy has good stress-corrosion resistance in HCl solutions and 0% HCl (distilled water). In fact, in a previous study [9], $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy was found only susceptible to stress-corrosion cracking in 100% H_2SO_4. This is probably attributed to the presence of enough passive alloying elements, Ni and Mo, in the glass as compared to the Fe-B-Si glasses. In the case of the MEES technique for detecting the susceptibility of SCC of the metallic glasse, detailed results will be given in the presentation.

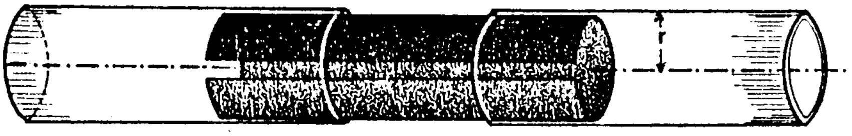

Figure 1: Schematic diagram of ribbon sample bent in the glass tubes.

TABLE 1
Stress corrosion of the $Fe_{78}B_{13}Si_9$ glass

	Time to failure (hrs)			
strain x 10^{-3} (mm/mm)	25% HCl	50% HCl	75% HCl	100% HCl
3.34	≤ 2.5	≤ 1.5	≤ 1	≤ 3.5
4.0	≤1.5	≤ 1.5	≤ 1	≤ 3.5
8.35	≤ 1.5	≤ 1	≤ 0.25	≤ 3.5
11.13	≤ 1	≤ 1	≤ 0.25	≤ 3.5

TABLE 2
Stress corrosion data of the $Fe_{81}B_{13.5}Si_{3.5}C_2$ glass.

	Time to failure (hrs)			
strain x 10^{-3} (mm/mm)	25% HCl	50% HCl	75% HCl	100% HCl
4.62	≤ 1.5	≤ 5.5	≤ 0.25	≤ 3.5
5.8	≤ 1.5	≤ 5.5	≤ 0.25	≤ 3.5
11.55	≤ 1	≤ 1	≤ 0.25	≤ 3.5
15.4	≤ 1	≤ 1	≤ 0.25	≤ 3.5

TABLE 3
Stress corrosion data of the $Fe_{66}Co_{18}B_{15}Si_1$ glass

	Time to failure (hrs)			
strain x 10^{-3} (mm/mm)	25% HCl	50% HCl	75% HCl	100% HCl
4.0	≤ 1.5	≤ 5.5	≤ 1	≤ 3.5
5.0	≤ 1.5	≤ 5.5	≤ 1	≤ 3.5
10.0	≤ 1.5	≤ 5.5	≤ 0.25	≤ 3.5
13.3	≤ 1	≤ 1.5	≤ 0.25	≤ 3.5

TABLE 4
Stress corrosion data of the $Fe_{77}B_{16}Cr_2Si_5$ glass

	Time to failure (hrs)			
strain x 10^{-3} (mm/mm)	25% HCl	50% HCl	75% HCl	100% HCl
3.34	≤ 2	≤ 1.5	≤ 1	≤ 3.5
4.8	≤ 2	≤ 1.5	≤ 1	≤ 3.5
8.35	≤ 1	≤ 1.5	≤ 0.25	≤ 3.5
11.13	≤ 1	≤ 1.5	≤ 0.25	≤ 3.5

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