

#### Abstract:

Bulk metallic glass (BMG) materials are a <u>newn almost newly\_introduced</u> class of glassy alloys with amorphous structure and a superior combination of properties, such as high mechanical strength, good thermal stability, a large supercooled super cooled liquid region, potential for easy forming, and good corrosion resistance, and magnetic properties. Within the Among all numerous BMG systems developed and studied so far, Fe-, Ti-, and Zr-based BMG have the highest amount most numbers of research topics because of due to their noticeable potential for biomedical applications and corrosion wear resistance. H is well known that In addition to the beside the mechanical tolerance of of the biomaterials materials to be used as biomaterials, there are some other critical ideascriteria for need to be considerationed, such as corrosion resistance, chemical stability, and biocompatibility of the materials. Overall, the paper discusses In this paper, the current research status of investigations on the corrosion resistance and biocompatibility\_of\_the current well-known BMG-salloys is reviewed. Furthermore, it The comprehensive-reviews current BMGs'-p resents the effect of different elements and their microstructures (crystallinity, and the effects they have on ) on electrochemical behavior, environments, and corrosion mechanisms, of most of the currently developed BMGs in different environments and conditions with an overview on the involving mechanisms.

#### 1. Introduction

For the last two decades, mMetallic glasses werehave been the subject of numerous studies researches for the last two decades. They have exhibited shown superior mechanical properties such as (strength and hardness), soft magnetic characteristics, damping properties, high wear resistance and great oxidation/corrosion resistance in different environments [1] [2]. These properties have resulted in their a variety of extensive possible applications for in structural and functional materials

The fabrication and processing of bulk metallic glasses (BMGs are created by d) ecreasing are based on retarding the crystalline structure formation and through through control of ling the phase transformation phase for of certain these alloys [3]. In addition, the a-Ability to form final complicated shapes is a another significant properties feature of BMG alloys. BMG alloying systems are typically cheing eategorized in ferrous and non-ferrous alloy groups. Ferrous alloys usually contain Fe, Co and Ni, while non-ferrous BMGs consist of a wider range of base elements like Zr, Ti, Hf, Pd, Ca, Cu, Pt and Au. Currently, the variety of number of introduced bulk glassy alloys have passed one thousand and continues to growit is growing more, as well [1].

In order for For the stabilization of super\_cooled liquids to stabilize and fabricate and other fabrication considerations, there are three primary rules these BMGs\_should be produced regarding three primary rules[3]. Firstly, they typically must consist of more than three alloying elements,

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#### Abstract:

Bulk metallic glass (BMG) materials are a new class of glassy alloys with amorphous structure and a superior combination of properties such as mechanical strength, thermal stability, a super cooled liquid region, easy forming, corrosion resistance, and magnetic properties. Within the BMG systems, Fe-, Ti-, and Zr- have the highest amount of research because of their potential for biomedical applications and corrosion resistance. In addition to the mechanical tolerance of biomaterials, there are other ideas for consideration such as corrosion resistance, chemical stability, and biocompatibility. Overall, the paper discusses current research on corrosion resistance and biocompatibility of well-known BMGs. Furthermore, it reviews current BMGs' elements and their microstructures crystallinity, and the effects they have on electrochemical behavior, environments, and corrosion mechanisms.

#### 1. Introduction

For the last two decades, metallic glasses were the subject of numerous studies. They exhibited superior mechanical properties such as strength and hardness, soft magnetic characteristics, damping properties, and corrosion resistance in different environments [1] [2]. These properties resulted in a variety of possible applications for structural and functional materials.

BMGs are created by decreasing the crystalline structure formation and through control of the transformation phase for certain alloys [3]. In addition, the ability to form final complicated shapes is a significant feature of BMG alloys. BMG alloying systems are typically categorized in ferrous and non-ferrous alloy groups. Ferrous alloys usually contain Fe, Co and Ni, while non-ferrous BMGs consist of a wider range of base elements like Zr, Ti, Hf, Pd, Ca, Cu, Pt and Au. Currently, the variety of bulk glassy alloys passed one thousand and continues to grow [1].

In order for super cooled liquids to stabilize and fabricate, there are three primary rules [3]. First, they typically must consist of more than three alloying elements, and have a reasonable potential for suppressing phase transformation. Second, at least 12% atomic size between three main elements must mismatch. Third, the elements must exhibit negative heat mixing. In addition to the primary rules, a multicomponent system always belongs to an eutectic structure. This facilitates the production of the glassy alloys. Finally, we will focus on the compositions near the eutectic point with the lowest melting temperature.

The BMGs possess a variety of properties compared to other crystalline alloys. The combination of properties and processing capabilities give them potential for comparison to other currently used alloys. In some cases, BMGs demonstrate even better features such as:

- strength
- ductility
- elastic modulus

and to have a reasonable potential for suppressing phase transformation. Second, <u>at least there should be at least 12%</u> atomic size <u>between three main elements must</u> mismatch, <u>between three main elements Third</u>, and the last requirement is the <u>elements must exhibit</u> negative heat\_s of mixing among the elements. <u>In addition to the primary rules</u>, <u>It can also be declared that a multicomponent system with having these rules</u> always belongs to an eutectic type structure system. This <u>will</u> facilitate the production of the glassy alloys. <u>Finally</u>, <u>win which we willean</u> focus on the compositions near the eutectic point with the lowest melting temperature.

The BMGs possess a <u>variety-wide range</u> of considerable properties compared to other conventional crystalline alloys. The combination of these properties and their processing capabilities have given them the potential for to be compacomparisonred to other currently used alloys. <u>I and in some cases</u>, <u>BMGsthey</u> demonstrate even better features <u>such as. Some of these</u>:

• properties are mechanical properties (strength

- \_\_\_\_\_ductility
- fracture toughness
- and fatigue e),
- biomedical
- biocompatibility
- —,electrochemical and corrosion resistance

e [4]. Awhich all of the features them were have been studied and evaluated for various types of glassy alloys [4].

In previous corrosion resistant studies, BMGs gained attention for their distinct Among different properties and characteristics\_of metallic glassesincluding excellent, corresion resistance study of BMGs has been drawn a wide attention during the past years, due to excellent electrochemical properties of these alloy systems in different solutions and mediumsa. For As an instance, in various corrosive environments, the corrosion resistance of some Co, Ni, and Fe based bulk metallic glasses is have been reported to be supposedly -100 to 1,0000 times better than the populare most used -corrosion resistant-stainless steel (SUS 316L) in various corrosive environments [1]. Knowing the corrosion characteristics of BMG becomes even more significant when they are to be utilized for biomedical or decorative applications such as (jewelry and watches, watches etc.), or when the surface behavior has a critical importance. Because Since the microstructural defects <u>such aslike</u> grain boundaries, <mark>and precipitates or secondary phases</mark>, and inclusions are not present in the structure of glassy metals, uniform and homogenous passive layers with very low weak points might can be formed on their surfaces. As a result, and this helps promote the resistance to chemical and corrosion attacks, as well [5]. In addition to the Beside the structural homogeneity of glassy alloys, there exists a potential of adding various certain appropriate elements potentially to increases the corresion resistance vity to corresion for in these amorphous systems. Other sStudies have suggest hown that the addition of Mo, Cr, and Win Fe-P-C metallic glass mighteen drastically increase the resistance to the corrosion drastically [6] [7] [8]. Also Among the wide range of BMGs electrochemical studies, Cr containing alloys and also-Zr-based Vitreloy (Vit1) alloy familiesy exhibithave been reported to show excellent corrosion resistancent in saline solutions when compared to with crystalline metallic alloys [9] [10].

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- fracture toughness
- fatigue
- biomedical
- biocompatibility
- electrochemical and corrosion resistance

All of the features were studied and evaluated for various types of glassy alloys [4].

In previous corrosion resistant studies, BMGs gained attention for their distinct characteristics including excellent electrochemical properties in different solutions and mediums. For instance, in various corrosive environments, the corrosion resistance of some Co, Ni, and Fe based bulk metallic glasses is supposedly 100 to 1,0000 times better than the popular stainless steel (SUS 316L) [1]. Knowing the corrosion characteristics of BMG becomes even more significant when utilized for biomedical or decorative applications such as jewelry and watches, or when the surface behavior has a critical importance. Because microstructural defects such as grain boundaries, precipitates or secondary phases, and inclusions are not present in the structure of glassy metals, homogenous layers with very low weak points might form on their surfaces. As a result, this helps promote resistance to chemical and corrosion attacks [5]. In addition to the structural homogeneity of glassy alloys, adding certain elements potentially increases the resistance to corrosion for amorphous systems. Other studies suggest that the addition of Mo, Cr, and Win Fe-P-C metallic glass might drastically increase the resistance to corrosion. [6] [7] [8]. Also, Cr containing alloys and Zr-based Vitreloy (Vit1) alloy families exhibit excellent corrosion resistance in saline solutions when compared to crystalline metallic alloys [9] [10].

So far, most of the studies on metallic glasses concentrate on fabrication, glass forming ability (GFA), and their mechanical properties. Other experiments were conducted on conventional metallic glasses [1] [3]. However, since the chemical compositions of BMG glasses and their processing are typically different with the earlier ones, there is a need for a comprehensive, established review about the electrochemical and corrosion properties of amorphous bulk alloys and the influential factors on their characteristics.

So far, most of the studies on metallic glasses have been concentrated on their fabrication, glass forming ability (GFA) and their mechanical properties. Other and some experiments investigations were conducted on have also been done on thin conventional metallic glasses, as well [1] [3]. However, since the chemical compositions of BMG glasses and their processing are typically different with the earlier ones, there is a need for a comprehensive, established review about the electrochemical and corrosion properties of these amorphous bulk alloys and the influential factors on their se-characteristics.

Many So far, a number of review papers have been\_reviewed the manufacturing process and their mechanical properties very well [1] [3] [11]. However, their main focus is not have been barely about the corrosion properties of BMG alloys in various conditions. In the present paper, an iMy purpose is to nelusive reviewfocus on of recent investigations on about chemical and electrochemical characteristics of the most popularknewn BMG systems in their various conditions and environments. Throughout the paper, well-known BMG alloys are compared based on their properties such as will be presented and the corrosion behavior of different known BMG alloys will be compared. The review includes will consist of recent electrochemical and corrosion studies on different alloys, and their compositional systems in various environments.

### 3.2. Ferrous BMG alloys

#### 3.1-2.1. Fe-based Bbulk Mmetallic Gglasses and Ttheir Ceorrosion Pproperties

In 1974, First reports on the electrochemical studies about of amorphous melt-spun Fe-based Fe-Cr-P-C alloy was published. in 1 It include information about 974 and high corrosion resistance in HCl solutions, was reported for that system [12] [13]. After the introduction of first Fe based amorphous BMG in 1995, bulk metallie glasses (BMGs) based on F with Fe bases are the most have been come out as the most popular amorphous alloys among the researchers because of due to their unique combination of characteristics. Like high strength and hardness, high glass transition temperature, good wear resistance, soft magnetic properties and also great corrosion resistant in aggressive media [11]. In addition, fabrication and processing of Fe-based BMGS are more cost effective than the other glassy, metallic alloys with based on Zr, Co, Ni, Ti, Co, Mg, Pt, orand Au bases. This makes, making them attractive for large scale productions. As previously mentioned mentioned before, Fe-based BMG lack certain the microstructural features such as grain boundaries and precipitates. Tthey possess a chemically homogenous surface structure that is resistant to corrosive species [3]. Within the microstructure, The electrochemical properties are ean be even more enhanced optimized through the introduction of ing specificappropriate elements such as Cr and Mo into the microstructure. In other studies, Some reports have shown that similar to stainless steels, Cr is the most influential element when in increasing iron-based, amorphous alloys' corrosion resistance [14] [15]. Furthermore, In an study in 1N NaCl solution at 30°C the Fe-Cr crystalline specimens were corroded at a rate of about 0.5-1 mm/year, while the amorphous Fe-Cr-P-C alloy corrosion rate was tsoo small to be numerically measured [12]. Other Another interesting experiments observation include was related to the weight changes evaluation of weight changes in of glassy Fe-based alloys when in various concentrations of HCl (from 0.01 to 1N). -For a week, the Fe-based alloys that was almost zero for were the exposedesure of 1 week toin a solution at 30°C. Even though it is well-known that, while

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So far, most of the studies on metallic glasses concentrate on fabrication, glass forming ability (GFA), and their mechanical properties. Other experiments were conducted on conventional metallic glasses [1] [3]. However, since the chemical compositions of BMG glasses and their processing are typically different with the earlier ones, there is a need for a comprehensive, established review about the electrochemical and corrosion properties of amorphous bulk alloys and the influential factors on their characteristics.

Many papers review the manufacturing process and mechanical properties very well [1] [3] [11]. However, their main focus is not about the corrosion properties of BMG alloys in various conditions. My purpose is to focus on recent investigations about chemical and electrochemical characteristics of the most popular BMG systems in their various conditions and environments. Throughout the paper, well-known BMG alloys are compared based on their properties such as the corrosion behavior. The review includes recent electrochemical and corrosion studies on different alloys, and their compositional systems in various environments.

### 2. Ferrous BMG alloys

### 2.1. Fe-based Bulk Metallic Glasses and Their Corrosion Properties

In 1974, one of the first reports on the electrochemical studies about amorphous, melt-spun Febased Fe-Cr-P-C alloy was published. It include information about high corrosion resistance in HCl solutions. [12] [13]. After the introduction of first Fe based amorphous BMG in 1995, BMGs with Fe bases are the most popular amorphous alloys among researchers because of their unique combination of characteristics. In addition, fabrication and processing of Fe-based BMGS are more cost effective than the other glassy, metallic alloys with Zr, Co, Ni, Ti, Co, Mg, Pt, or Au bases. This makes them attractive for large scale productions. As previously mentioned, Fe-based BMG lack certain microstructural features such as grain boundaries and precipitates. They possess a chemically homogenous surface structure that is resistant to corrosive species [3]. Within the microstructure, electrochemical properties are enhanced through the introduction of specific elements such as Cr and Mo. In other studies, similar to stainless steels, Cr is the most influential element when increasing iron-based, amorphous alloys' corrosion resistance [14] [15]. Furthermore, 1N NaCl solution at 30°C the Fe-Cr crystalline specimens were corroded at a rate of about 0.5-1 mm/year, while the amorphous Fe-Cr-P-C alloy corrosion rate was too small to be numerically measured [12]. Other interesting experiments include the evaluation of weight changes in glassy Fe-based alloys when in various concentrations of HCl (from 0.01 to 1N). For a week, the Fe-based alloys were exposed to a solution at 30°C. Even though it is well-known that austenitic (crystalline) stainless steels are susceptible to severe pitting when exposed to HCl and Cl environments [13].

it is well known that austenitic (crystalline) stainless steels are susceptible to <u>severe sever</u> pitting when exposed to in HCl and Cl eentaining environments [13].

The good resistance of Fe-Cr-based amorphous alloys resistance to corrosion is has been attributed to the formation of a protective hydrated chromium oxyhydroxide passive layer on its the surface sastainless steel, and Because as a result of Fe-Cr is a stainless steel and has anits amorphous structure, its passive layer showcases a results in higher resistance to corrosion compared to other with Cr based alloys stainless steel, with a similar Cr content [16]. For comparison, Fig. 1 shows the a-mass losts 4comparison between Fe<sub>67.7</sub>B<sub>20</sub>Cr<sub>12</sub>Nb<sub>0.15</sub>Mo<sub>0.15</sub> BMG and a crystalline stainless steel with the same amount of Cr soaking in H<sub>2</sub>SO<sub>4</sub> solution [17].

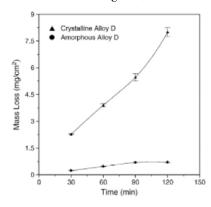


Figure 1 shows the -m-Mass losses resultsting from the immersion of amorphous and crystalline Fe67.7B20Cr12Nb0.15Mo0.15 alloys in a 0.1 M H2SO4 solution [17].

## 2.1.1. Effect of Aalloying Eelements 3.1.1.

As discussed before, one of the primary elements used in various alloys' compositions is Cr. The addition of Cr. As mentioned earlier, helps increase the resistance to corrosion, erosion, or metallic dissolution—one of the primary elements used in various alloys compositions in order to increase the resistance to corrosion/erosion and metallic dissolution is Cr. Cr is the main element for the formation of passive protective film over a wide range of alloys. Similar to crystalline alloys, Cr was has been introduced to the BMG amorphous alloys in order to improve their corrosion behavior in aggressive environments.

In a study by J. Jayraj et al. <u>studied</u> [18] <u>the</u> Fe<sub>43</sub>Cr<sub>18</sub>Mo<sub>14</sub>C<sub>15</sub>B<sub>6</sub>Y<sub>2</sub>Al<sub>2</sub> BMG alloy <u>was studied</u> under <u>the</u> conditions that simulated <u>a</u> bipolar plate. <u>The alloy was suspended</u> in polymer electrolyte membrane fuel cell (PEMFC) by means of potentiodynamic and potentiostatic polarization <u>experiments</u>. <u>Thand the</u> results were compared <u>to with that of SUS316L</u>. <u>Under PEMFC</u> environments, Fe-based BMG show<u>sed</u> the <u>bestsuperior</u> corrosion resistance compared <u>to with the SUS316L</u> (Fig. 2).

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Fe-Cr-based amorphous alloys' resistance to corrosion is attributed to the formation of a protective hydrated chromium oxyhydroxide passive layer on its surface. Because Fe-Cr is a stainless steel and has an amorphous structure, its passive layer showcases a higher resistance to corrosion compared to other Cr based alloys. [16]. For comparison, Fig. 1 shows the mass lost between Fe<sub>67.7</sub>B<sub>20</sub>Cr<sub>12</sub>Nb<sub>0.15</sub>Mo<sub>0.15</sub> BMG and a crystalline stainless steel with the same amount of Cr soaking in H<sub>2</sub>SO<sub>4</sub> solution [17].

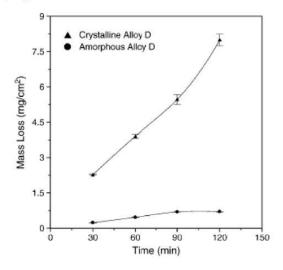


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J. Jayraj et al. studied [18] the Fe<sub>43</sub>Cr<sub>18</sub>Mo<sub>14</sub>C<sub>15</sub>B<sub>6</sub>Y<sub>2</sub>Al<sub>2</sub> BMG alloy under conditions that simulated a bipolar plate. The alloy was suspended in polymer electrolyte membrane fuel cell (PEMFC) by means of potentiodynamic and potentiostatic polarization. The results were compared to SUS316L. Under PEMFC environments, Fe-based BMG shows the best corrosion resistance compared to SUS316L (Fig. 2).