

Corrosion behaviour of bulk $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ amorphous alloy and its crystallized form

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Bulk amorphous alloys are a very interesting class of materials because they own exceptional properties or combinations of properties which can not be achievable by conventional crystalline materials. Fe-based amorphous alloys are known to have high strength and hardness, excellent soft magnetic properties and high corrosion resistance. It was of great interest to analyze the behavior of amorphous alloys during anodic polarization in concentrated salt solutions and in the salt-fog test. Bulk $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ amorphous alloys in form of rods with the diameter of 1 mm and 20 – 35 mm in length were synthesized by copper mould casting method. Electrocorrosion in 3% NaCl and salt fog tests were performed for the bulk amorphous alloy and for its crystalline counterpart.

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1. Introduction

Fe-based bulk metallic glasses (BMGs) are regarded as having a high potential for industrial applications, due to the high availability and relatively low cost of the main alloying element, Fe, and their outstanding properties, e.g. high strength, elastic modulus and hardness, in part very good magnetic properties, and expected high corrosion resistance, which are not achievable by conventional crystalline alloys [1-4].

From the beginning of amorphous metals, a large number of research studies had been devoted to the development of Fe-based amorphous alloys with excellent corrosion-resistant properties. It was especially observed that several of those can exhibit corrosion resistance superior to that of stainless steels [5-6]. For example, exceptional resistance was demonstrated for amorphous Fe-Cr-Mo-metalloid alloys with distinct compositions which passivate spontaneously even in hot concentrated hydrochloric acid or Fe-Ni-Cr-Mo-B alloys which exhibit excellent passivation behaviour in acid solutions, up to 250°C [7].

But this first generation of amorphous Fe-based alloys possessed only low glass forming ability and thus, could be obtained only as thin or small products e.g. ribbons, foils, powders or films. In order to overcome the size limitation of this first generation, the second generation of alloys that are bulk glass-formers was recently developed. However, most of them were predominantly designed for attaining other properties, e.g. for combining high GFA and excellent mechanical performance, rather than for corrosion resistance [8-9].

Therefore, these alloys have substantially different compositions compared to earlier ones, e.g. they contain reactive Mn, and have usually lower concentrations of beneficial Cr and P. Although, those compositional variations are expected to have quite a critical influence on

long term stability under applicative conditions, the corrosion behavior of bulk glassy Fe-based alloys has been scarcely studied so far [7-10].

Ideally, amorphous alloys are regarded as being structurally and chemically homogeneous. They are free from secondary phases or inclusions which could initiate the corrosion processes. However, in practice, the presence of defects in cast samples could not be completely avoided, at least in commercial production. Not surprisingly, several studies revealed that some BMGs have high pitting susceptibility and pits are initiated at the interface between such defects and the surrounding matrix. Furthermore, amorphous alloys can be regarded as single-phase solid solutions, often exceeding the solubility limits of alloying elements at equilibrium [11-12].

2. Experimental procedures

Bulk $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ amorphous alloys in rod form with the diameter of 1 mm and length of 20 - 35 mm were prepared by copper mould casting method, as presented in Fig. 1.



Fig. 1. Amorphous rod obtained by copper mould casting.

The amorphous structure of the elaborated samples was examined by X-ray diffraction (XRD) using a DRON

3 diffractometer, with the radiation of a Mo anode with wavelength $\lambda = 0.71 \text{ \AA}$. In the diffraction pattern (Fig. 2) can be observed only broad peaks which indicates that the sample has an amorphous structure.

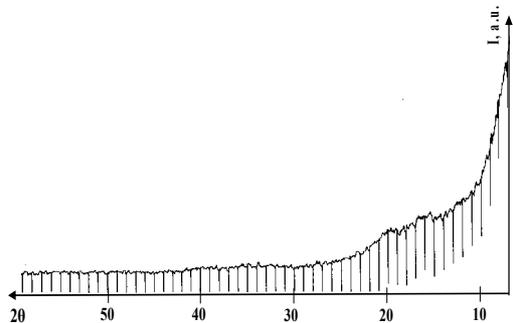


Fig. 2. XRD pattern for the cast bulk $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ alloy sample.

The corrosion behavior of this bulk amorphous alloy was compared to its crystalline counterpart. The crystalline counterpart was obtained by an annealing heat treatment of the amorphous alloy at a temperature higher than the crystallization temperature. Two types of experiments were performed: linear voltammetry and salt fog testing. In order to achieve a high reliability of the results, all the measurements were repeated at least two times. The electrochemical experiments were carried out at room temperature, by a three electrode cell assembly of 250 ml and a potentiostat/galvanostat EG&G (model 273) connected to a computer by a GPIB card and controlled by the software Corrview. The samples were placed as working electrode, a graphite bar was used as counter electrode, and silver – silver chloride (Ag/AgCl) electrode as a reference. The parameters related to the corrosion resistance, specifically the corrosion current density (i_{corr}) and the potential of corrosion ($E(I=0)$), were obtained using the software Corrview. The potential applied was $\pm 200\text{mV}$ in open circuit and the scanning speed was 2 mV/s . Following the analysis were determined the polarization curves, which represent the change of current density depending on the potential applied.

The electrochemical parameters values associated to electrochemical corrosion process were obtained by extrapolation of Tafel curves. The salt fog test is the oldest way of determining the corrosion resistance and most widely used for highly corrosion resistant materials, becoming a universal test. One of the advantages of this test is that a wide range of materials can be tested and test duration is short compared to the environment. The solution used is a solution of 5% mass NaCl (higher content than seawater). Process temperature is kept at 35°C and the pH ranging from 6.5 to 7.2. After the salt fog test, the samples were analyzed using a VHX-600 KEYENCE 3D digital microscope.

3. Results and discussions

The corrosion behaviour of $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ bulk amorphous alloy and its crystallized form was

determined by linear voltammetry tests in 3% NaCl solution. In a linear voltammetry experiment, the voltage applied to the circuit varies from two potentials, one maximum positive and one maximum negative, with a constant gradient variation. The values obtained from corrosion tests in 3% NaCl are presented in Table 1.

Table 1. Parameter values of corrosion test in 3% NaCl.

Alloy	Corrosion potential [V]	Current density [$\mu\text{A}/\text{cm}^2$]	Corrosion rate [mm/year]
$\text{Fe}_{67}\text{Cr}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{Mo}_4\text{C}_4$ as quenched	0,556	4,917	0,721
$\text{Fe}_{67}\text{Cr}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{Mo}_4\text{C}_4$ crystallized	0,357	7,649	1,123

Comparing the values of the current density of the tested samples, it can be noted that i_{corr} decrease from $7.649 \mu\text{A cm}^{-2}$ (crystallized state) to $4.917 \mu\text{A cm}^{-2}$ (amorphous state). This shift of current density values to small values indicates improved corrosion behaviour. Hence, the amorphous alloy sample has a better corrosion resistance.

The polarization curves were obtained by determining the current density change depending on the applied potential in time, Fig. 3. As it can be observed, the corrosion potential of as quenched $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ sample was swept to more positive value compared to the corrosion potential of its crystallized part, which indicates that the amorphous sample has a better corrosion resistance.

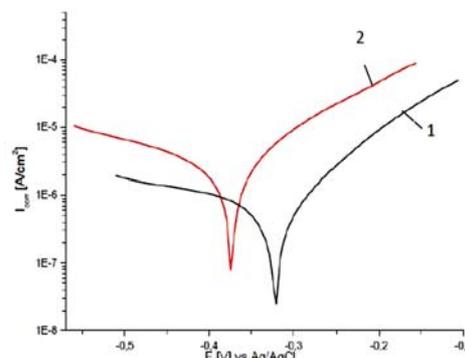


Fig. 3. Polarization curves of samples tested in 3%NaCl, 1 - $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ as quenched; 2 - $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ crystallized.

In Fig. 4 it is presented the corrosion rate for both structural states, calculated using Faraday equation (according to ASTM G 59 and G 102). According to this equation, it was obtained a corrosion rate of 0.720 mm/year for the $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ sample as quenched and 1.1 mm/year for its crystallized part. It can be observed a decrease of the corrosion rate of about 40 % for the as quenched sample compared to the crystallized state.

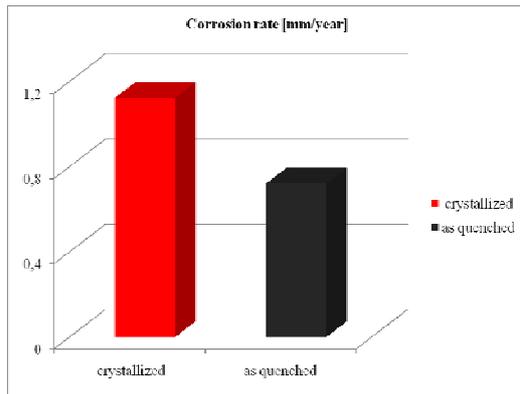
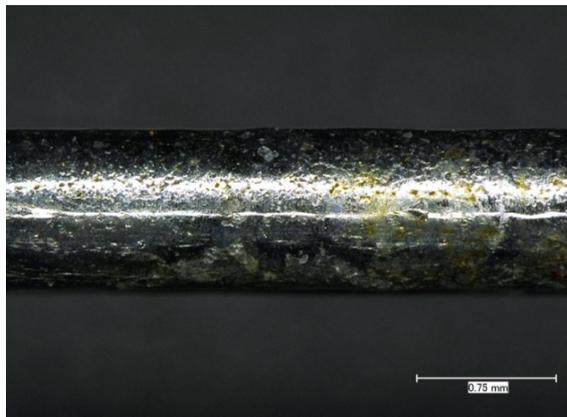


Fig. 4. Corrosion rates of the tested samples

Salt spray tests were carried out in a salt spray fog chamber in the laboratory of Materials Science at the University of Applied Sciences Gelsenkirchen, Germany. Specimens of bulk $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ amorphous alloy and its crystallized state were hanged in the chamber using nylon threads. This procedure kept each specimen electrically isolated from the surroundings. The samples were maintained for 48 hours in a corrosive environment with a concentration of 1 M NaCl. Following the salt spray test, the amorphous sample preserves its metallic glow, unlike the crystalline alloy that shows visible signs of rust (Fig. 5).



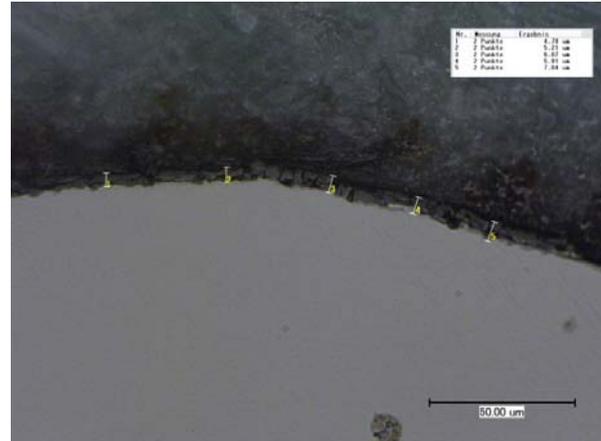
a)



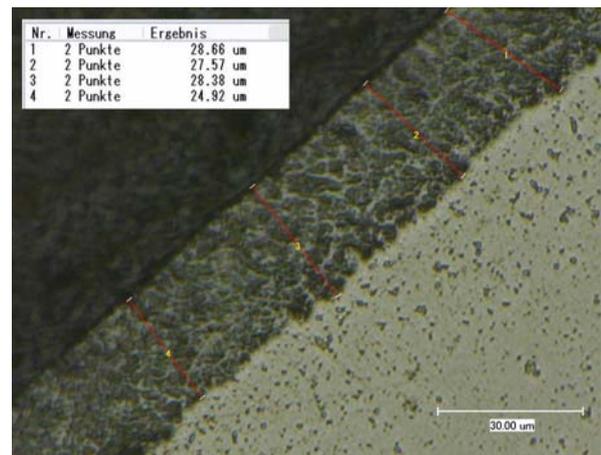
b)

Fig. 5. The corroded Samples, a) $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ as quenched; b) $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ crystallized/

The corroded layer thickness was measured with the 3D digital microscope at a magnification of 2500x (Fig. 6). The average thickness of the corroded layer for the amorphous sample is 6 μm and for the crystallized sample is 27 μm . It can be noticed an improvement in corrosion resistance of the amorphous sample, almost four times better than its crystallized form.



a)



b)

Fig. 6. Corroded layer thickness for, a) $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ as quenched; b) $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ crystallized.

4. Conclusions

Bulk $\text{Fe}_{67}\text{Cr}_4\text{Mo}_4\text{Ga}_4\text{P}_{12}\text{B}_5\text{C}_4$ amorphous alloys and its crystallized form samples were tested to corrosion resistance in salt spray and linear voltammetry experiments. Based on the results of the linear voltammetry experiments of amorphous and crystalline samples in 3% NaCl can be concluded that the amorphous structure is more resistant to corrosion. The corrosion rate measured for both states decreased to almost 40% for the as quenched state compared to its crystalline state. Salt fog-testing showed improved resistance to corrosion of the amorphous alloy, four times better than its crystallized state.

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