

Plasma electrolytic polishing of bulk metallic glasses: what determines success?

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Abstract

In this study two types of bulk metallic glasses (BMG) were treated by plasma electrolytic polishing (PEP). Namely Vitreloy 101 with chemical composition Cu-Ti-Zr-Ni and AMZ4 with chemical composition Zr-Cu-Al-Nb. Both types of samples were manufactured by means of a laser powder bed fusion (PBF-LB/M) technology. In addition, AMZ4 samples were prepared using two distinct PBF-LB/M parameter sets. Owing to the similar chemical composition of the BMGs, they underwent the PEP-treatment in the same electrolytes. Surprisingly, different AMZ4 samples responded to it differently, whilst the results obtained on Vitreloy 101 samples were reproducible and predictable when process parameters and/or electrolyte were modified. Furthermore, some AMZ4 samples broke during or shortly after the PEP-treatment as they became more brittle and/or their surface became strongly oxidised. On the other hand, the Vitreloy 101 samples showed no signs of degradation and their surface became more glossy and smooth after the PEP-treatment. Nevertheless, it must be mentioned that for some AMZ4 samples satisfactory results were obtained, as they did not disintegrate during the process and/or did not break immediately after it and their surface became smoother and glossier. This inconsistency in the response to the same treatment of the same material could be attributed to the varying surface oxidation level of the AMZ4 samples and/or not yet properly selected electrolyte(s). The PEP duration varied from $\tau = 300$ s to $\tau = 600$ s with applied voltage between $U = 300$ V and $U = 420$ V. The pH value of the electrolyte varied between 3.4 and 3.8 during the PEP process and the electric conductivity was $\kappa \approx 105$ mS/cm at electrolyte temperature of $t = 75$ °C.

Plasma electrolytic polishing; bulk metallic glasses; additive manufacturing; surface oxidation; hatching strategy

1. Introduction

Material science is on an ongoing quest to develop new more durable, more mechanically stable and/or biocompatible, etc. materials. Recently a metastable austenitic CrMnNi steel was presented that demonstrates both increased yield and tensile strength and improved ductility at the same time [1], [2]. Bulk metallic glasses (BMGs), however, have been known since 60s'. The vitrification of metals with various chemical compositions were achieved by rapid quenching [3]. The benefits of hardness, increased elastic limits and biocompatibility sparked the interest for using BMGs for a number of different applications ranging from medical engineering to sports [4]. Recently, successful attempts to produce BMGs, namely Vitreloy 101 and AMZ4, by means laser powder bed fusion (PBF-LB/M) were reported [5]–[9]. It is well known, that the size of BMG parts is constricted by the precise cooling rate of a bulk material at which the vitrification takes place [3], [5]. A successful application of additive manufacturing (AM) technologies in producing BMGs, relaxes this constraint [5].

However, it is well established, that the surface quality of additively manufactured parts is rather poor. This, in many engineering applications, and customary preferences, is a serious drawback limiting parts applicability. Of course, there is

a number of techniques to refine the surface of AM parts, like particle blasting, (dry) electrochemical polishing, mechanical polishing etc. All these methods with greater or lower efficiency can be applied on AM parts made out of conventional material, like steel or titanium alloys [10]–[12]. Yet BMGs like Vitreloy 101 and AMZ4 pose a challenge to all of these polishing methods, especially to those exploiting electrochemistry. The chemical composition of these materials is very complex, thus an electrolyte used in such processes must be well tailored to avoid selective material removal, or other kind of surface damage. Furthermore, the unique material properties vanish upon crystallisation, which limits the temperature window during the post processing. Since cast BMGs typically feature a very good surface finish, and PBF-LB/M just recently emerged, studies on post-treatments are limited to a few exemptions.

Though there is a research gap on polishing BMGs, few studies have emerged reorting the efficiency of successful plasma electrolytic polishing (PEP) of BMGs [13]–[15].

In this study, results on PEP of AMZ4, a Zr-based alloy, and Vitreloy 101, a Cu-based alloy, are presented. The selection of the used electrolyte and PEP process parameters is discussed. The effect of the surface quality, namely the existing oxide film on as-received samples, is determined by the achieved polishing results. The efficacy of the PEP treatment is evaluated in terms of an area surface roughness S_q , a root mean square height,

and S_v , a maximum pit height, as it is shown to influence the fatigue life of AM parts the most [16].

2. Material and methods

2.1. Plasma electrolytic polishing

A bath-PEP technology where samples are immersed into the electrolyte bath was used for post-processing additively manufactured AMZ4 and Vitreloy 101 samples with different surface quality in as-received condition. The principal scheme of the test rig is presented in [17]. The applied direct voltage, U , was varied in the range from 300 V to 420 V. The electrolyte temperature, t , was varied from 75 °C to 85 °C. The process time, τ , was varied from 300 s to 600 s.

An electrolyte for Zr-based alloys was prepared following the chemical composition of an electrolyte used for polishing Zr-based bulk metallic glasses as reported in [13]. Yet, the Vitreloy 101 samples were also polished in this electrolyte. As it will be discussed later in this article, the polishing results of the AMZ4 samples were not reproducible, thus some additives, e.g., surfacants were added.

Due to the hydrodynamic conditions occurring during the bath-PEP process that is not assisted by an electrolyte stream directed to a specific sample surface, samples might be exposed to a different intensity of the PEP process. In other words, the efficiency of the treatment depends on the sample orientation in the electrolyte. In order to achieve as uniform as possible polishing effect, all samples were polished in two-steps, i.e. after half of the PEP time, τ , the samples were rotated by 180° and continued to be polished.

2.2. AMZ4 and Vitreloy 101 samples

Owing to the success of the previous experience in PEP-treating Vitreloy 101+Sn [15], only few test samples out of Vitreloy 101 were used for the PEP treatment in this study. Thus, the main focus of this article is placed on polishing the AMZ4 samples. It is acknowledged that the chemical compositions of AMZ4, which is a Zr-based material, i.e. Zr-Cu-Al-Nb, and Vitreloy 101, which is a Cu-based material, i.e., Cu-Ti-Zr-Ni, are rather different. Yet, the Vitreloy 101 samples were also polished in AMZ4-specific electrolyte(s).

In total four types of the AMZ4 samples were PEP-treated. They are so categorised according to the used PBF-LB/M-parameters and/or additional surface treatment using the particle blasting (PB) technique, which resulted in different surface quality of the analysed samples. Figure 1 shows the characteristic AMZ4 and Vitreloy 101 samples used in this study.

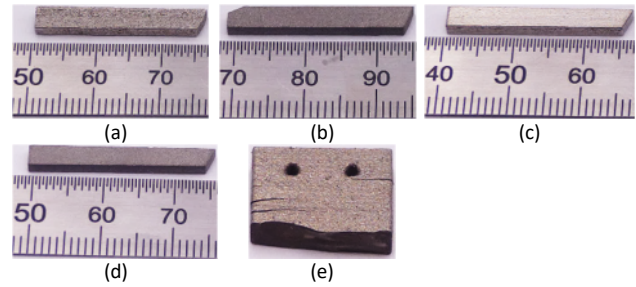


Figure 1. Characteristic AMZ4 samples manufactured using (a) standard PBF-L/M settings, (b) additional contouring strategy, (c) standard PBF-L/M settings with PB, (d) additional contouring strategy + PB and (e) Vitreloy 101 sample in as-received condition.

The characteristic measurements of the samples dimension and mass were taken before and after the PEP process. For these measurements a digital micrometer *BGS technic 8427* (resolution 0.001 mm), a digital electronic calliper (resolution 0.01 mm) and a scale *KERN 572* were used. The surface roughness of the samples before and after the PEP treatment was measured by a confocal microscope *MarSurf CM Explorer*.

3. Results and discussion

The PEP process conditions are listed in Table 1. One can see that the current during the PEP process, when the standard electrolyte was used, is significantly higher compared to the modified electrolyte. This is because the experiments using the basic electrolyte were conducted in a three times lower electrolyte volume. Note that the electric conductivity of both electrolytes was $\kappa \approx 105$ mS/cm at $t = 75.0$ °C.

Table 1 PEP process parameters investigated in this study and resulting surface roughness S_q and S_v .

Sample No.	Sample class	Electrolyte	PEP time, τ , s	Voltage, U , V	Current, I , A	Temperature, t , °C
1	Standard	Base	600	331	4.0	79.4
2			600	328	4.0	79.2
3			600	328	4.0	79.6
4	Contour		600	329	4.0	79.7
5			600	329	4.0	79.4
6			300	330	4.0	77.8
7	Standard	Additives	600	300	2.5	74.6
8			600	300	2.3	74.7
9			600	300	2.5	74.4
10	Contour		600	300	1.5	75.0
11			600	300	3.6	75.4
12			300	300	1.0	84.8
13	Standard+PB		600	420	1.1	84.7
14			600	300	2.1	74.9
15			600	300	2.1	74.6
16	Contour+PB		600	300	2.5	74.8
17			300	300	2.3	74.9
18			300	300	2.5	74.1
19	Contour	600	300	2.2	75.3	
20		600	360	1.1	84.2	
21		600	360	1.1	84.7	

Figure 2 presents the selected samples after the PEP. One can see that the surface of Sample 5, which was treated in a basic electrolyte, was ruined since a dark oxide layer was formed on it during the treatment. Sample 1, on the other hand, which was PEP-treated at the same conditions developed no signs of degradation. Furthermore, the initial surface roughness of both samples, as shown in Figure 3, was comparable. Remarkably, the surface roughness of both samples was reduced by the PEP process, regardless of the developed oxide layer on Sample 5. Note that surface roughness of all the investigated samples was measured on the same sample side, in the middle of the sample in $2.3 \times 2.3 \text{ mm}^2$ area.

From Figure 3, one can see that the surface roughness could consistently be reduced when samples were polished in a basic electrolyte, while using the modified electrolyte the surface roughness, especially S_v parameter, would increase/decrease unpredictably. One can argue that these results could have been affected by the applied voltage. Indeed, samples polished in a basic electrolyte were exposed to $U \approx 330 \text{ V}$, while samples polished in the modified electrolyte were exposed to $U = 300 \text{ V}$,

except a few samples polished at 360 V and 420 V. However, samples that were polished in the basic electrolyte at $U = 300 \text{ V}$ broke, thus they are not further discussed in this article.

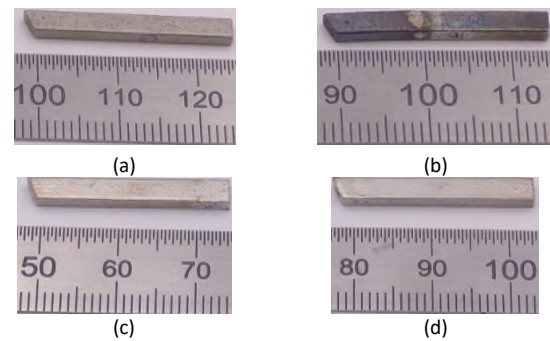


Figure 2. Photographs of (a) Sample 1, (b) Sample 5, (c) Sample 20 and (d) Sample 21 after PEP.

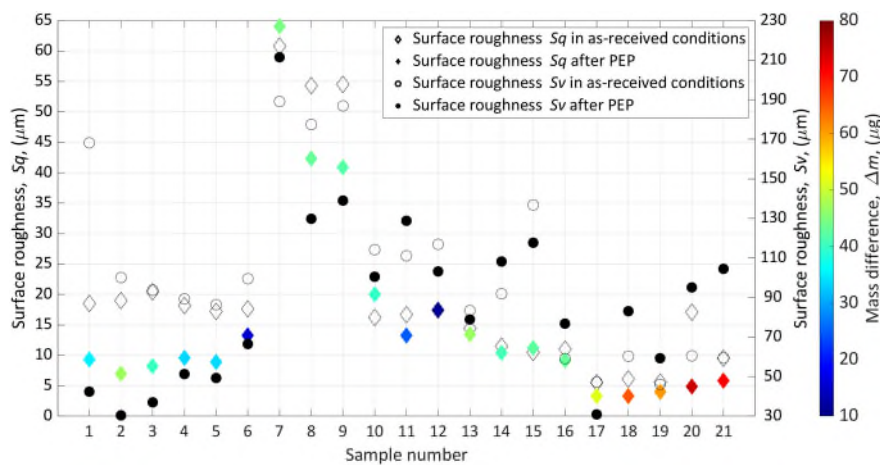


Figure 3. Surface roughness S_q and S_v before and after PEP. The colour scale shows the mass difference before and after PEP.

Further investigation of the surface topography of the samples before and after the PEP revealed that PEP uncovered some defects of the PBF-LB/M process causing artificial increase in surface roughness. These defects, like weld tracks and/or lack of fusion, partly molten particles etc. create artificial surface valleys/peaks that are evaluated as surface roughness. Some examples of such surface defects are highlighted with red arrows in Figure 4. Nevertheless, the duration of the PEP treatment for Sample 9 and other samples, which were manufactured using the standard PBF-LB/M parameters and had higher initial surface roughness compared to those that were produced with contour scanning strategy and/or additionally particle blasted could have been extended to achieve lower surface roughness. The surface quality of the samples with already low initial surface roughness, on the other hand, was significantly improved in $\tau = 300 \text{ s}$ of PEP.

Finally, it must be reported that multiple samples that were polished in a base electrolyte broke during or shortly after the PEP and/or developed black oxide layer as shown in Figure 2 (b). A very few samples, that are reported in Table 1 were successfully polished in this electrolyte. Initial hypothesis was that the samples had a light oxide layer that prevented a good electrical contact with the power source. Thus a new batch of samples with improved surface quality, i.e. after particle blasting, was produced. Indeed, a light oxide layer on the samples with standard manufacturing parameters was indicated under the microscope. A trial test was performed on one sample

with improved surface quality in the base electrolyte and it was ruined. Thus the initial hypothesis was disregarded and a modified electrolyte was developed and used for polishing the rest of the samples. However, the phenomena of the modified electrolyte was rather temporary. At a certain point, samples polished in this electrolyte also started to develop a black oxide layer. Fortunately, no sample broke during or shortly after the PEP treatment. Despite the continuous modulation of the pH level and the electrolyte conductivity, no successful PEP experiments could be conducted at $U = 300 \text{ V}$. Thus, several trials at higher applied voltage, as reported in Table 1, were carried out that astonishingly led to positive results. However, the reason behind this is not yet understood. The Vitreloy 101 samples, though, could be successfully polished using both electrolytes at varying process conditions without any signs of sample degradation.

4. Conclusions

In this study two electrolytes were tested for PEP of AM AMZ4 and Vitreloy 101 samples. The AMZ4 samples were prepared using two distinct PBF-LB/M process parameter sets. Part of these samples were also particle blasted. These samples were PEP-treated using various process settings and the obtained results are summarised as follow:

1. The efficacy of the PEP process on AMZ4 / Vitreloy 101 does not depend on the initial surface oxide layer.

- The results obtained using the base electrolyte for PEP of AMZ4 are not reproducible.
- The degeneration of the modified electrolyte was slowed down by added surfactants. Yet, the damage to the surface of the polished AMZ4 samples could be avoided only by modulating the process parameters rather than electrolyte properties.
- Vitreloy 101 samples could be successfully polished in either of the electrolytes without any signs of damage to the surface.

Future studies will focus on a wider PEP parameters in terms of electrolyte temperature and applied voltage to determine the right set of parameters for post-processing BMGs materials. The crystallisation of the samples as well as mechanical properties of the PEP-treated AMZ4 samples will be investigated to find out whether PEP influences the material properties.

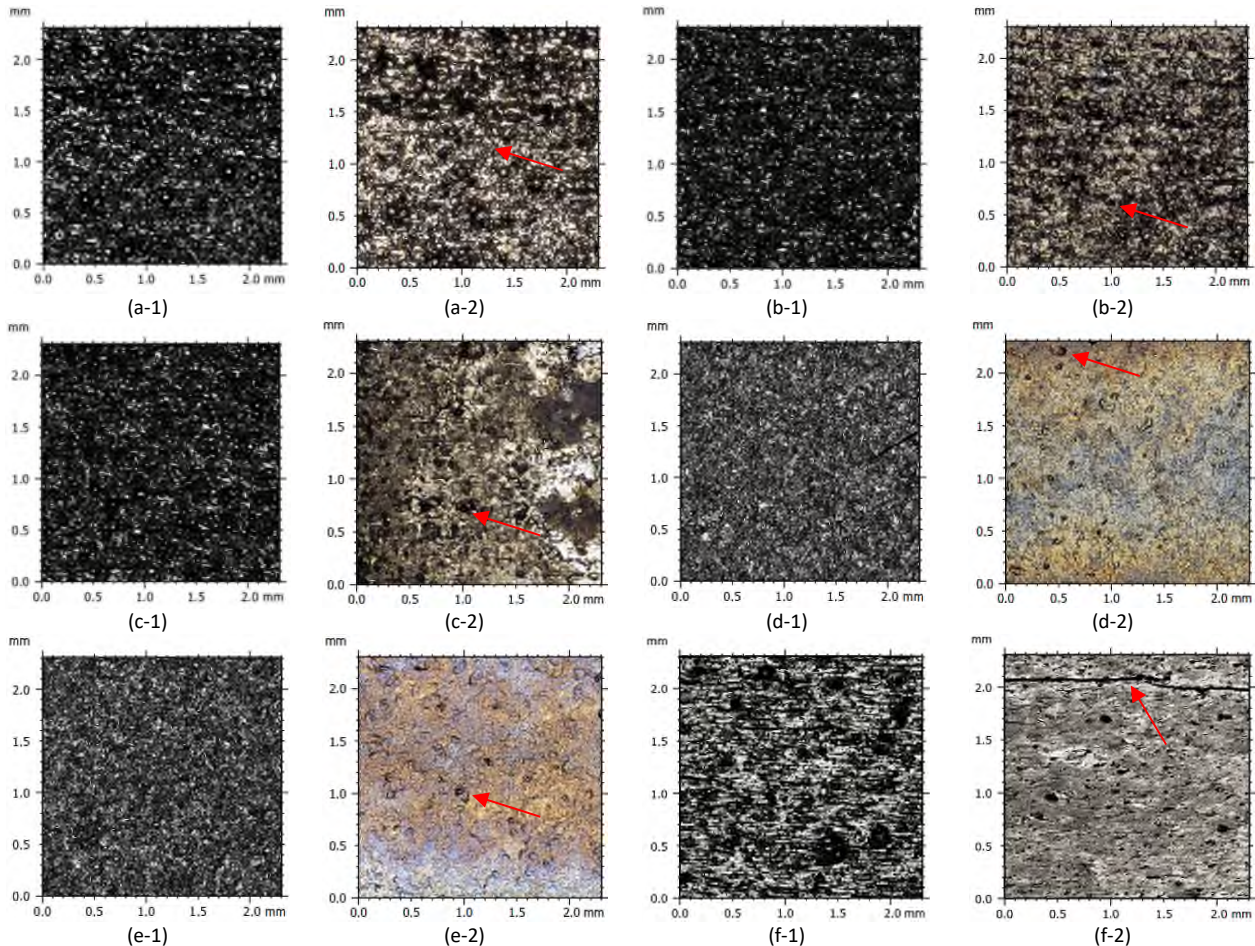


Figure 4. Micrographs of analysed samples in (1) as-received and (2) after PEP conditions: (a) Sample 9, (b) Sample 10, (c) Sample 11, (d) Sample 17, (e) Sample 18 and (f) Vitreloy 101.

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