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## 1 **Microstructure and corrosion study of Fe-based bulk metallic glass obtained by Spark** 2 **Plasma Sintering**

3  
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### 13 14 **Abstract**

15 Due to the necessity of developing new materials with better anti-corrosive properties, bulk  
16 metallic glasses are the focus of many research projects. In this study, a metallic glass with  
17 Fe<sub>48</sub>Cr<sub>15</sub>Mo<sub>14</sub>C<sub>15</sub>B<sub>6</sub>Y<sub>2</sub> composition was produced by high-pressure atomization spray and  
18 densified by Spark Plasma Sintering. Different sintering cycles, temperatures, and pressures  
19 were carried out to conserve the amorphous structure while increasing its density. The  
20 temperatures used for this study were below the glass transition temperature, and the uniaxial  
21 force was varied between 50 to 400 MPa. Amorphous samples with nearly 98 % of relative  
22 density were obtained. The effect of the sintering cycle used on the phase transformation and  
23 microstructure of the materials was studied. Additionally, the porosity and crystallinity were  
24 related to the corrosion resistance properties through electrochemical characterization.

25  
26 **Key Words:** Spark plasma sintering; Metallic glass; Corrosion resistance.

30

## 31 **1. Introduction**

32 Metallic glasses are increasing interest in academic researches and industry. They are  
33 electronically and optically like ordinary metals, but the absence of crystals and defects as  
34 vacancies, dislocations, or grain boundaries increase their chemical, physical and mechanical  
35 properties [1]. These materials could be used in a wide range of fields. They can be used to  
36 develop magnetic devices, microsystems, or for aeronautical or biomedical applications. The  
37 absence of grain boundaries provides high mechanical strength and corrosion resistance,  
38 making these materials an ideal candidate to stand up to aggressive environments depending  
39 on their composition [2–4].

40 Metallic glasses have been developed as powders, ribbons, and small pieces [2,3,5,6].  
41 Coatings of metallic glass have also been studied by different deposition techniques [7–9].  
42 However, new processing techniques that allow manufacturing larger pieces of bulk metallic  
43 glasses (BMGs) are still needed. Spark plasma sintering (SPS) is an advanced sintering  
44 technique for consolidating powders into nanostructured bulk materials. It has been recently  
45 used in broader applications and has gained a strong reputation as a versatile method for  
46 solid-state processing of metals, ceramics, and composites. The ease in parameter  
47 manipulation in SPS makes this process beneficial for the preservation of amorphous  
48 structures. [10]. Some studies have been performed to study the use of SPS in metallic glass  
49 processing [11,12]. They found that SPS can increase the specimens' size produced by a  
50 conventional copper mold casting in diameter and with a higher fracture strength.

51 One of the challenges to fabric BMG is to keep the amorphous structure on the materials.  
52 However, still unresolved if fully dense materials with some crystallinity percentage have  
53 higher corrosion resistance than a completely amorphous one with lower density.

54 Among the variety of BMGs, Fe-Cr-based bulk metallic glasses have attracted much attention  
55 because of superior corrosion resistance, high strength, and hardness. Like stainless steel, a  
56 concentration of Cr above 8 at.% leads to the growth of a passive film that protects the  
57 material from aggressive environments [13–15]. However, Fe-Cr-based BMGs exhibit  
58 almost no plastic strain and strain hardening even in compression when tested at room  
59 temperature, restricting their applicability [16]. In this study, SPS's effects on the  
60 densification, crystallinity, porosity, and corrosion properties of a Fe-Cr-Mo-C-B-Y metallic  
61 glass alloy are investigated to guide future SPS developments of Fe-Cr bulk metallic glasses.

## 62 **2. Experimental**

### 63 *2.1. Metallic glass powder preparation*

64 The appropriated amounts of high purity elemental materials (> 99.9 %) were used to produce  
65 the mother alloy with a final atomic composition of  $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Y}_2$ . The 2 at.% of  
66 yttrium was added to the metallic composition because it enhanced the glass-forming ability  
67 [17,18]. The alloy was home-made by convection melting under an argon atmosphere, and  
68 the metallic glass powder was obtained by high-pressure spray atomization. After  
69 atomization, the powder was sieved until 43  $\mu\text{m}$  mesh.

### 70 *2.2 Spark Plasma Sintering parameters and characterization*

71 Three different sintering cycles were selected to vary the samples' density while searching to  
72 conserve the amorphous phase. The first sintering cycle (S1) used a heating rate of 50 °C/min  
73 until the final temperature (Tf) with 15 minutes of holding time at this temperature. Cycle  
74 two (S2) used an initial heating rate of 50 °C/min until Tf-15 °C and a heating rate of 1°C/min  
75 until Tf. Cycle 3 (S3) used an initial heating rate of 50 °C/min until Tf-30 °C and a heating  
76 rate of 1°/min until Tf.

77 The tests were performed in a commercial SPS (Fuji-SPS, japan) equipment using 7 g of  
78 powder, a tungsten carbide died of 15 mm of diameter, and Grafoil® as a protective film  
79 between the died and the powder. The final temperature was fixed at 575 °C, below the glass  
80 transition temperature (Tg) of this alloy (577 °C); the uniaxial force used for the test was 50  
81 MPa. It worth mentioning that the Tg of this alloy was measured at a heating rate of  
82 10 °C/min and the heating rate during the sintering process starts at 50 °C/min, which causes  
83 an increase in the Tg according to the works of T. Paul et al. [19,20].

84 The samples obtained by the three different sintering cycles were analyzed by XRD, SEM,  
85 and the density was measured by the Archimedes method. After the results of the three  
86 different sintering cycles were obtained, the one with better properties respecting the  
87 amorphous phase of the material was selected and used for the subsequent tests where the  
88 temperature and the uniaxial force were variated. All the samples obtained were analyzed by  
89 X-ray diffraction (XRD), and their densities were measured as well by the Archimedes'  
90 method. Table 1 reports the sample names and the SPS pressure and temperature used in this  
91 work. Note that the parameter selection is explained later in the document.

92

93 *2.3 Electrochemical test*

94 The electrochemical tests were performed in the samples obtained from the three different  
95 sintering processes and the sample obtained after the variables' optimization. Before the test,  
96 the samples' surface was polished until SiC 1200, and the roughness was measured by a 2D  
97 profilometer using the JIS1994 standard in a Surfcoeder SE300 (Kosaka Lab, Japan). Average  
98 values were given for three profiles.

99 The electrochemical characterizations were carried out in a typical three-electrode glass cell.  
100 The working electrode was the sample with an average surface of 1.10 cm<sup>2</sup> in contact with  
101 the solution. The real surfaces were determined by optical surface measurements (Keyence  
102 One Shoot microscope) before corrosion tests. A graphite rod (5 cm<sup>2</sup>) and a Mercury Sulfate  
103 Electrode (MSE,  $0V_{MSE} = +0.650 V_{ENH}$ ) were used as a counter electrode and the reference  
104 electrode, respectively. Corrosion tests were performed in a naturally aerated sodium sulfate  
105 solution (10 g/L) at pH 6.5 (no buffer solution and room temperature). This solution was  
106 preferred to NaCl to avoid pitting, which can be sensitive to crystallinity, porosity, and the  
107 roughness of the materials. Electrodes were connected to an SP-300 potentiostat equipped  
108 with a low current probe (Biologic, France). Open circuit potential (OCP) was first recorded  
109 for 3 hours to ensure the potential stability and the passive film steady state.

110 Electrochemical impedance spectroscopy measurements were then performed at the OCP  
111 with a frequency range of 100 kHz to 10 MHz with 9 points per decade and signal amplitude  
112 of 5 V<sub>rms</sub>. The electrochemical characterizations were completed by linear sweep  
113 voltammetry. A reduction step was performed from the OCP to  $-0.7 V_{MSE}$ , and then the  
114 potential was reversed to  $-0.3 V_{MSE}$ . The scan rate was fixed to 1 mV/s. Only the

115 potentiodynamic curves from  $-0.7 V_{MSE}$  to  $-0.3 V_{MSE}$  are shown here since the forward and  
116 backward cathodic currents overlap.

#### 117 *2.4 Characterization techniques*

118 The powder was analyzed by X-ray Diffraction (XRD) apparatus from  $30$  to  $80^\circ$  in  $2\theta/\theta$   
119 mode with a step of  $0.5^\circ$  /min using Cu-K $\alpha$  radiation at 40 kV and 40mA. The granulometry  
120 analysis was performed in dry by laser diffraction using a Malvern equipment (LMS-3000).  
121 The morphology of the particles was analyzed by SEM (Hitachi SU-70) coupled with an EDS  
122 probe (SDD Apollo XL). Differential scanning calorimetry (DSC) analysis was performed  
123 in a Rigaku apparatus at a heating rate of  $10^\circ\text{C}/\text{min}$  from  $300$  to  $700^\circ\text{C}$ . After corrosion  
124 tests at the OCP, a surface analysis was conducted by XPS analysis (Quantum 2000 apparatus  
125 (ULVAC-PHI, Inc). A  $100\ \mu\text{m}$  spot monochromatic Al K $\alpha$  source ( $1486.7\ \text{eV}$ ) in constant-  
126 analyzer-energy mode (pass energy  $187.85\ \text{eV}$  for wide scan and  $58.7\ \text{eV}$  for regions) was  
127 selected to record the spectrum of Fe2p, Cr2p, and Mo3d. Details of the analysis are given  
128 later.

### 129 **3. Results and discussion**

#### 130 *3.1 Metallic glass powder, obtaining and Sintering.*

131 The powder obtained by induction oven and gas atomization (Figure 1a) has mainly spherical  
132 morphology particles mixed with elongated particles typical of this processing method, as  
133 shown in figure 1a. After a sieving process, the particle size showed a lognormal distribution  
134 with an average particle size ( $Dv_{50}$ ) of  $24\ \mu\text{m}$  (Figure 1b). Particle size has been shown to  
135 affect the densification process during spark plasma sintering. Smaller particle sizes increase

136 the contact areas and have stronger driving forces increasing the mass migration, which  
137 benefits the densification [21,22]. The mean particle size used in this work is similar to the  
138 smaller reported for other authors with the same composition [23,24]. Even if sieving was  
139 performed, the particle distribution was relatively wide, as confirmed by a SPAM of 1.5. The  
140 X-ray diffractogram (Figure 1c) on the powder shows a significant and broad peak,  
141 characteristic of the amorphous structures [25].

142 The DSC test (Figure 1d) shows a glass transition temperature ( $T_g$ ) of 577 °C and two  
143 exothermic peaks, which correspond to two crystalline temperatures  $T_{x1}$  and  $T_{x2}$ , at 653 and  
144 670 °C, respectively, and a supercooled liquid region ( $\Delta T = T_x - T_g$ ) of 76 °C. T. Paul et al. [26]  
145 studied the sintering mass mechanism of a similar amorphous alloy powder by SPS. They  
146 found the densification's onset, which is around 320 °C. The maximum densification rate  
147 attended was at ~ 585 °C retaining its amorphous structure. Additionally, they corroborate  
148 that the dominant mass transport mechanism during sintering is by viscous flow. On the other  
149 hand, A. Shing et al. [27] sintered the same alloy at a temperature close to the  $T_g$  (570 °C).  
150 They found that it leads to a notable atomic reordering and the formation of medium-range-  
151 ordering (MRO) clusters. However, this formation of nanocrystals could reduce the  
152 propagation of the shear bands during deformation, increasing the material's hardness. S.P.  
153 Harimkar et al. [24] also reported crystallization during SPS at temperatures below the  $T_x$   
154 and close to the  $T_g$ . Therefore, to avoid devitrification, temperatures below the  $T_g$  were used  
155 for this work.

156 Figure 2 shows the sintering cycles applied to the metallic glass powder to produce BMG  
157 samples. The cycles S1 and S2 almost overlap even if they do not exactly follow the same

158 steps. For S1, the maximum temperature (575 °C) was reached in one step with a 50 °C/min  
159 heating rate. Because of the SPS's temperature control system (PID), the maximum  
160 temperature was overtaken for a short period (~2 min). To avoid it, the cycle S2 was designed  
161 to reach (i) 560 °C with a heating rate of 50 °C/min and then (ii) 575 °C with a heating rate  
162 of 1 °C/min. For the cycle S3, the powder was heated up to 555 °C with a rate of 50 °C. Then,  
163 the temperature of 575 °C was reached with a 1 °C/min heating rate. With this procedure, the  
164 cycle S3 took 15 min more than S1 and S2. Note that the materials' sintering time has an  
165 important role since it can induce crystallization or crystal growth [24,28]. The samples  
166 obtained after SPS had a diameter of ~14 mm and a thickness of ~10 mm. They were labeled  
167 as S1, S2, and S3, depending on the sintering cycle used.

168 XRD patterns on S1, S2, and S3 samples are reported in figure 3a. The diffractograms show  
169 the coexistence of amorphous and crystalline structures with a ratio that depends on the SPS  
170 cycle. Thus, S1 presents the highest degree of crystallization, while S3 remains mostly  
171 amorphous. According to figure 3a, S2 presents an intermediate behavior. For S1, two kinds  
172 of carbides precipitates were identified:  $(\text{Fe, Cr})_{23}(\text{B, C})_6$  (ICDD 98-061-2585) and  
173  $\text{C}_1\text{Cr}_2\text{Fe}_{14}$  (ICDD 98-007-6800). The S2 diffractogram shows similar peaks as S1  
174 characteristics of carbides but with lower intensity, suggesting a higher ratio of the  
175 amorphous phase. After cycle S3, the sample remains mostly amorphous with low-intensity  
176 peaks characteristics of chromium iron carbide  $\text{C}_1\text{Cr}_2\text{Fe}_{14}$ . The samples' crystallinity  
177 percentage was calculated with the formula proposed by M. Ohlberg et al. [29] for partially  
178 devitrified glasses using the X-ray diffractograms. The crystallinity obtained in the samples  
179 is 70 %, 24 %, and 19 % for S1, S2, and S3, respectively, with a standard deviation of  $\pm 5$  %.

180 The samples' density (Figure 3b) showed the highest value for sample S2 with 87 %,  
181 followed by the S1 sample with 85 % and S3 with 83 %. Even though the final temperature  
182 was the same for the three cycles, the sintering heating rate affects the material's activation  
183 energy. The sintering time of sample S3 is longer than the other samples, due to the very  
184 slow heating rate, but the crystallinity percentage of the sample is the lowest as well as the  
185 density (Figure 3). This phenomenon was also observed by L. H. Liu et al. [30]; they found  
186 out that the behavior of viscous flows is different during SPS sintering; slow rates of heating  
187 increase the activation energy for mass transportation as it is demonstrated with a lower  
188 density in sample S3. Tanaji Paul et al. [31] predicted the viscous flow activation energy  
189 dependence on the heating rate by the Arrhenius equation and the directional structural  
190 relaxation model, demonstrating a viscosity dependence on the heating rate at temperatures  
191 lower than the  $T_g$ . They modeled different heating rates and demonstrated that the activation  
192 energy decreases with the heating rate's increments.

193 Additionally, to this effect, it should be considered the effective time at the final temperature.  
194 Sample S1 had a holding time of 15 min at the maximum temperature, which can induce  
195 devitrification, and with it, an increase in the viscosity affecting the densification process.  
196 Tanaji Paul et al. [32] studied the effect of SPS annealing on a BMG Fe-based alloy's  
197 crystallization behavior with a similar composition to the one used in this work. They  
198 established that during the annealing time, the pre-existing nuclei grow into well-developed  
199 crystals, and the increase in the duration of isothermal annealing causes an increase in the  
200 volume fraction of all crystal sizes in the material. It implies that during the sintering cycle  
201 S1, crystals were formed during the heating process and grew during the holding time.

202 Figure 4 shows the SEM top surface images of the edges, the centers, and the cross-section  
203 of samples S1, S2, and S3. The micrographs of the edge top surface (Figure 4a) show that  
204 the particles are in an initial sintering stage where their morphology is almost as in the initial  
205 state suggesting local bonding mechanisms in the outer region. This area still is very porous.  
206 In the center of the sample (Figure 4b), metallic glass particles merge more or less well as a  
207 cycle function. The morphology of the particles is no longer observed in samples S1 and S2.  
208 However, in sample S3 their morphology is still distinguishable. However, they have already  
209 formed and grown necks during the sintering process. S3 sample have an evident porosity,  
210 which is not observed in S1 and S2 samples. Finally, in the cross-section micrographs (Figure  
211 4c), it can be observed how the densification changes in each sample. In S1 sample it can be  
212 observed different degrees of sintering. It has areas where the particles are totally cohered  
213 and others where they just have necks formation. In the S2 sample, it is observed higher  
214 densification on the top than in the center. The particles in the top are cohered with some  
215 remaining porosity while in the center of the sample, still possible to observe the particles'  
216 morphology, and the sample is very porous. S3 sample shows a more homogeneous sintering  
217 degree between the top and the center, but it is more porous than samples S1 and S2.

218 The difference of densification between the edge and the center observed for all the samples  
219 in the micrographs (the centers are higher densified than the edges) and a difference in density  
220 from the top to the center is a direct consequence of the establishment of two gradients of  
221 temperature in the SPS mold. The first gradient is axial from the bottom to the top surface of  
222 the sample. The second gradient is radial from the center to the edge of the sample. Note that  
223 the gradient amplitude is modified by the diameter and thickness of the sample produced.  
224 According to Tanaji et al. [33], for a similar composition of metallic glass as this work, the  
<https://doi.org/10.1016/j.jallcom.2021.160399>.

225 radial temperature gradient during SPS for a die of 15 mm is  $\sim 29$  °C between the center and  
226 the die wall (where the thermocouple is located) when a heating rate of 100 °C/min is applied.  
227 The  $\Delta T$  is directly proportional to the heating rate; for a heating rate of 50 °C/min, the  
228 temperature gradient is  $\sim 14.5$  °C.

229 On the one hand, S1 presents the highest degree of cohesion between the grain, a relative  
230 density of 85 %, and a crystallinity ratio of 70 %. On the other hand, SEM images on S3  
231 show particles not entirely interconnected in the center of the sample, consistent with the low  
232 relative density (about 83 %) and a low degree of crystallinity (19 %). The sample S2 presents  
233 a compromise between the densification, the particle's cohesion, and the crystallinity degree.

234 Even if S2 presents an average behavior, further material optimization was performed from  
235 the sintering cycle S3. Indeed, the crucial point is to keep the amorphous structures of the  
236 alloys.

### 237 *3.2 Optimization of BMG materials*

238 In SPS, the applied pressure during the process aids in particle arrangement. It enhances the  
239 sintering kinetics, while the temperature enhances the atomic motion, and with it, the  
240 diffusion process, but in metallic glasses, also promotes crystallization. Note that the  
241 temperature should be above 535 °C of a Fe-alloy to activate particle deformation playing a  
242 role in the material densification [34]. Therefore, the final temperature was decreased at  
243 560 °C to avoid crystallization, but the axial pressure of samples S4 was increased from  
244 50 MPa to 100, 200, 300, and 400 MPa. Additionally, to reduce the axial thermal gradient,  
245 the powder used was decreased from 7 g to 3.5 g.

246 X-ray diffractograms were recorded on the new samples with the conditions mentioned  
247 above. Figure 5a reports the X-ray pattern for each pressure. It is worth noticing that the  
248 crystalline phase observed previously at 575 °C and 50 MPa is no longer detected, with a  
249 maximum temperature of 560 °C. Therefore, a reduction of 10 °C of Tf is beneficial to keep  
250 the material's amorphous state. Whatever the pressure, only amorphous peaks are observed  
251 on diffractograms confirming that the higher sintering pressure does not affect the volume  
252 fraction of the amorphous phase until the temperature is carefully selected. Note that this  
253 trend may be alloy-dependent, as Maurya et al. [35] observed with the consolidation pressure  
254 of amorphous Al alloys by SPS.

255 Relative densities of the samples are reported as a function of the pressure in figure 5b. A  
256 linear increase in density is observed from 50 to 200 MPa. Above this pressure, the density  
257 stabilizes about 98 %. The improvement of the density with the pressure was already  
258 theoretically analyzed by Paul et al. [34] on Fe-based amorphous alloys. They stated that the  
259 compressive viscous flow deformation of the particles was pressure dependent. The increase  
260 in density is then obtained through plastic deformation, and the sliding of the grain  
261 boundaries occurs to a larger extent at higher pressures. The high density also results in the  
262 particle size distribution and the presence of small elements that easily fill the voids and  
263 reduce porosities [36]. In figure 6, SEM images of the Fe-alloy BMG samples at different  
264 uniaxial pressures are shown. In the images, we can observe the effect of the pressure on the  
265 densification in the specimens at 50 and 100 MPa; the particles are slightly interconnected,  
266 the morphology of the particles does not yet present a change. At these parameters, the  
267 sintering process is in an early stage. The micrography of the sample at 200 MPa, shows a  
268 high increment in densification compared with the two previous samples; at this pressure, the  
<https://doi.org/10.1016/j.jallcom.2021.160399>.

269 particles emerged just with a remaining porosity between them. This also confirms the results  
270 obtained for the relative density (Figure 5b). The samples at 300 and 400 MPa showed an  
271 increase in densification with just a few remnant porosities on the surface. However, the  
272 300 MPa sample has a denser surface, which is in coherence with the relative density results.  
273 The S4-300 sample's cross-section showed defects in the specimen due to particle's  
274 detachment during the cutting and polishing process and maybe due to a low cohesive force  
275 between them. The cross-section of the sample also shows a homogeneous density through  
276 the sample.

277 The 15 °C reduction in the final temperature resulted beneficial in preserving the material's  
278 amorphous phase but significantly affected the sintering process. With the same sintering  
279 cycle and pressure as sample S3, sample S4-50 decreased in density from 83 % to 69 %. The  
280 increase in applied pressure proved to be effective in mitigating this effect and enabling to  
281 obtain higher densities.

### 282 *3.3. OCP behavior and passive film composition*

283 Electrochemical tests were performed to evaluate the crystallinity and the relative density  
284 influence on the Fe-Cr BMG's corrosion resistance. These tests were performed on S1, S2,  
285 and S3 samples and compared with S4-300, in which any crystallization was observed by  
286 XRD and had the highest relative density and homogeneity of the produced samples. Note  
287 that reproducibility tests were carried out, and the results overlap well. Therefore, only the  
288 trend curves are reported below.

289 It must be noticed that the presence of a gradient density may affect the electrochemical  
290 response of the systems. Assuming no variation in the chemical composition along the  
291 sample diameter, the electrochemical reactivity of the surface should be affected by the  
292 roughness induced by the open pores at the surface; rough passive surfaces are more sensitive  
293 to localized corrosion than flat ones [37]. This phenomenon is increased if pores are  
294 interconnected. In the following, macroscopic electrochemical tests were performed,  
295 knowing that they may underestimate surface reactivity since a macroscopic behavior is  
296 recorded [38]. To further in the effect of edge-center porosity of samples, local  
297 electrochemical analysis should be applied, which does not fall under this paper's scope [39].

298 Figure 7a shows the Open Circuit Potential recorded on SPS samples in the aerated sulfate  
299 solution (neutral pH, room temperature, and stagnant condition). Whatever the sample, the  
300 steady-state potential is reached after  $1 \times 10^6$  seconds of immersion. S1 presents the most  
301 anodic value at about -0.4 VMSE, followed by S2 and S3 at about -0.45 VMSE. Note that  
302 the difference of 50 mV might not be significant since a slight deviation of the potential is  
303 still detected for S2 and S3. In Figure 7a, S4-300 present the most active potential at about -  
304 0.52 VMSE. For this sample, the dropout of potential was confirmed on reproducibility tests  
305 and always occurred below  $6 \times 10^4$  seconds. Note that this potential transient is not understood  
306 yet.

307 Yang et al. [40] already reported such a trend focusing on the content of Mo, Cr, and Iron at  
308 the oxide state. For experimental confirmation, XPS analyses were performed on SPS  
309 samples after immersion at the OCP. Fe2p, Cr2p, and Mo3d were recorded. XPS peak  
310 software was used to fit the XPS spectra (Figure 8). Based on the literature [41,42] and open

311 database *La surface.com*, Fe2p was split into two regions: 706-707 eV and 708-714 eV. The  
312 first region was assigned to Fe<sup>0</sup> metallic state, and the second region was attributed to Fe  
313 oxidic states. The Cr 2p peak consisted of three peaks at around 573-571 eV, 575-576 eV,  
314 and 577-578 eV for the metallic state, Cr<sup>3+</sup>, and Cr<sup>6+</sup> oxidic states, respectively. For the Mo  
315 3d spectra, six peaks were used. Two peaks between 227-228 eV and 230-231 eV  
316 corresponded to Mo<sup>0</sup> metallic state. Two other peaks at 228-229 eV and 233-234 eV were  
317 assigned to Mo<sup>4+</sup> oxidic state. Finally, the peaks between 231-232 eV and 234-236 eV were  
318 attributed to Mo<sup>6+</sup> oxidic state. Figure 8 illustrates the XPS fit results of the Fe 2p, Cr 2p, and  
319 Mo 3d peaks for S1 (70% of crystallinity) and S4 (1% of crystallinity). The atomic  
320 concentration of these metallic elements was calculated from the metallic and oxidic state  
321 areas, for Yang et al.[40], the amorphous state of the material facts on the quantity of Cr- and  
322 Mo- oxides in the passive. Therefore, the quantity  $\beta$  was calculated from equation 1. Results  
323 of Equation 1 are reported in Table 2. They show an increase in the quantity of Cr- and Mo-  
324 oxide species on the surface with the crystallinity reduction of the samples. Consequently,  
325 the differences in passive currents on polarization curves and EIS experiments could be  
326 expected.

$$327 \quad \beta = \frac{A_{Cr\ 2p} + A_{Mo\ 3d}}{A_{Cr\ 2p} + A_{Mo\ 3d} + A_{Fe\ 2p}} \quad \text{Equation 1.}$$

328 With the large concentration of carbon in the material, the formation of MxCy carbides and  
329 intermetallic compounds were detected by X-ray diffraction (Figure 3). Depending on the  
330 thermal treatment, the carbide concentration reduces from S1 to S4. Precipitation of carbides  
331 is known to create a depletion area in Fe, Cr around. These places are then less covered by a  
332 stable and chrome-enriched film and are easily attacked.

333 The oxidation state of Mo, Cr, and Fe suggests forming a complex oxide film with a  
334 chemistry that may depend on the degree of crystallinity and the Cr/Mo ratio [40,43]. This  
335 later information was not confirmed by our XPS analysis either because of the sample's  
336 roughness that affects the peak morphology or the immersion duration.

337

### 338 *3.5. Surface reactivity in sulfate solution*

339 Figure 7b reports the typical linear sweep voltammetry curves after 3 hours at the OCP.  
340 Tafel's fit was performed on polarization curves for maker positions at a minimum of 80 mV  
341 of the corrosion potential. EC-Lab software was used to calculate the corrosion potential  
342 ( $E_{\text{corr}}$ ), the current density ( $J_{\text{corr}}$ ) at  $E_{\text{corr}}$ , the Tafel constants ( $\beta$  and  $\beta_c$ ), and the corrosion rate  
343 (Table 2).

344 The corrosion potential,  $E_{\text{corr}}$ , follows the trend observed on OCP. The highest cathodic  
345 potential is attributed to S4-300, which is the optimized materials in terms of amorphous  
346 phase and density. On the opposite, S1 presents the most anodic potential. For Yang et al.  
347 [40], the crystallization of Fe-Cr metallic glass alloy results in stabilizing iron oxides instead  
348 of chromium or molybdenum oxides. As the surface chemistry change, modifications of the  
349 cathodic and anodic behavior are expected.

350 The cathodic reaction is under a mix charge transfer and mass transport limitation on Tafel's  
351 plots, as expected in a neutral, aerated, and stagnant solution. In table 2, the Tafel constants  
352  $\beta_c$  are in the range of 120 to 90 mV/decade, corresponding to the hydrogen evolution reaction  
353 [44]. Also, one can notice a decrease of  $\beta_c$  with sample amorphization. This evolution is

354 either due to hydrogen reduction or oxide film reduction [40,45]. For the former, crystallinity  
355 could play a role in the surface energy linked to the oxide layer's chemical composition and  
356 contribute to hydrogen reduction. For the latter, oxide reduction may occur during the  
357 cathodic polarization. Depending on the film chemistry, iron oxides may preferentially  
358 reduce compare to chromium or molybdenum oxides [46–48]. As the ratio of iron  
359 oxide/hydroxides is higher for S1 than S2-S3 and S4-300, the cathodic current is stronger.  
360 Consequently,  $E_{\text{corr}}$  shifts to anodic values.

361 A passive plateau is observed in the anodic domain for the samples except for S1 (current  
362 density at about  $500 \mu\text{A}/\text{cm}^2$ ). The passivation domain or pseudo passivation is in the range  
363 of the corrosion potential and  $-0.35 V_{\text{MSE}}$ . This behavior is in agreement with the literature,  
364 which reports that partial crystallization of an amorphous structure is detrimental for the  
365 nucleation and growth of a passive film as well as its protectiveness even if the passive film  
366 chemistry do not differ for the same material at the crystalline or amorphous state [41]. Above  
367  $-0.35 V_{\text{MSE}}$ , the transpassive region starts with the selective dissolution of iron and chromium,  
368 as observed on stainless steel passive film [49]. The oxide nature also accounts for corrosion  
369 resistance. Less anodic current is required to maintain the steady-state passive film on  
370 amorphous materials than on semi-crystalline ones (Figure 7b and values of  $\beta_a$  in table 2).  
371 Consequently, the corrosion rate can be mitigated when fully amorphous materials are  
372 produced.

373 After 3 hours of immersion, electrochemical impedance spectra (EIS) were recorded at the  
374 OCP. In figure 9, Nyquist diagrams are characterized by a pseudo-capacitive loop online with  
375 a passive film's growth in a sulfate solution. On the one hand, the semi-circle loop increases

376 with the amorphous state of the bulk material, evidencing the beneficial effect of amorphous  
377 surfaces for corrosion resistance as reported for other chemical composition [15,50]. On the  
378 other hand, S1 is characterized by a constant phase of 45° for low frequencies values  
379 associated with reactions limited by diffusion processes [51].

380 EIS diagrams were fitted using the two electrical equivalent circuits (EEC) reported in table  
381 2. Both EEC are made with a constant phase element (CPE),  $Q_{dl}$ , related to the space charge  
382 and double-layer capacitance of the passive layer parallel to a resistance,  $R_{ct}$ , which expresses  
383 the charge transfer resistance associated with the faradic processes of oxidation and reduction  
384 (Equation 2). The CPE was preferred to the ideal capacitor ( $C_{dl}$ ) because of the sample  
385 surface heterogeneities and roughness. Using Brugg's approximation, it is possible to  
386 estimate the space charge capacitance  $C_{sc}$  with Equation 3. For S1, the diffusion process at  
387 low frequency is modeled by a Warburg semi-infinite diffusion element where  $\sigma_1$  is the  
388 Warburg coefficient (Eq .4). Note that W is added in serial with  $R_{ct}$ . For both EEC,  $R_e$   
389 represents the electrolyte resistance.

390  $Z(f)_{CPE} = [Q_{dl} \cdot (2\pi f)^n]^{-1}$  Equation 2

391  $\frac{1}{2\pi(R_{ct} \cdot Q_{dl})^{1/n}} = \frac{1}{2\pi R_{ct} C_{dl}}$  Equation 3

392  $Z(f)_W = \frac{\sqrt{2} \cdot \sigma_1}{\sqrt{j \cdot 2 \cdot \pi f}}$  Equation 4

393 Table 2 lists the EEC fit results, whereas the lines plotted in figure 9 show the fit results.  $R_e$   
394 is in the range of 50 to 150 Ohm cm<sup>2</sup> for all the tests, which is expected for a sulfate solution  
395 at 10 g/L. The crystallinity state induces a polarization resistance increase confirming the  
396 underneath microstructure's role in the passive film grown [51–54].

397 For  $Q_{dl}$  and  $n$ , the results in table 2 show a significant difference between crystalline (i.e.,  
398 S1) and quasi amorphous structures (i.e., S2, S3, and S4-300).  $Q_{dl}$  is about a few hundred  
399  $Fs^{(n-1)} \text{ cm}^{-2}$  for crystalline samples and drops to a few ten  $Fs^{(n-1)} \text{ cm}^{-2}$  for the degree of  
400 crystallinity lower than 30 %. Note that  $C_{dl}$  follows the same trend. On the one hand, the  
401 parameter  $n$  is about 0.6, which is characteristic of limited reactions through nano-micro  
402 porous structures [55–57]. The transmission line model and its derivatives were proposed to  
403 consider the pore size geometry, distribution on the impedance in the absence of diffusion  
404 [58,59]. Some works also proposed quantifying the porosity properties (number, length,  
405 radius) from the impedance data [57,60,61]. These approaches fall under this work scope as  
406 this behavior was only found for the most crystalline sample.

407 On the other hand, the parameter  $n$  is at approximately 0.8 for the three other samples. The  
408 deviation from the ideal capacitor ( $n=1$ ) is attributed to the metallurgical defects (voids,  
409 vacancies) in the space charge volume and the surface morphology, which is not smooth  
410 since samples were only polished to SiC 4000. Morphological gradients also exist from the  
411 center to the samples' outer region (Figure 4) [48,62,63]. Therefore, the bulks' crystallization  
412 and its consequences on the passive film structure are detrimental to its intrinsic resistance  
413 and not only regarding its nucleation and growth, as seen before.

414 Regarding the corrosion properties of the four Fe-based samples, there is a significant effect  
415 of SPS parameters on the surface reactivity. Whatever the sintering cycle selected, an oxide  
416 layer grows on the alloy surface. If operating conditions are suitable for amorphous  
417 structures, the Cr and Mo content in the oxide layer increases instead of Fe. The surface  
418 becomes passives and is characterized by a steady-state current in the passive range of a few

419  $\mu\text{A}/\text{cm}^2$ . The passive domain is similar to all samples regardless of the iron content in the  
420 film, suggesting that the oxide layer is not only formed by chromium oxide but a dual or  
421 duplex oxide mixing Cr, Mo, and Fe. The tuning SPS parameter also has a consequence on  
422 the degree of porosity. It must be noticed that porosity increases with the degree of  
423 crystallinity.

424 Porosity and, more generally, surface defects are prone to localized corrosion phenomena. In  
425 a chloride-free environment, the general dissolution behavior of materials is only  
426 characterized. The metallurgical study showed an absence of homogeneity in the porosity  
427 distribution along the sample's diameters. Indeed, the SPS process is more efficient on the  
428 samples' center than on edge. This gradient of defects also has a consequence on corrosion  
429 behavior. As the porosity increases, the corrosion resistance of the material changes. In  
430 addition to the chemical composition of the oxide layer, the porosity on the surface (i.e.,  
431 roughness) and pore interconnection give suitable conditions for localized corrosion. If the  
432 oxide layer is not strong enough (no pure chromium oxide layer), dissolution can start more  
433 quickly. Further work should focus on the local electrochemical of SPS samples, comparing  
434 edge and center reactivities to go deep in the local effect of crystallinity, porosity on micro  
435 galvanic coupling with a denser and amorphous area of the sample.

#### 436 **4. Conclusions**

437 Spark plasma sintering is a technique that facilitates the processing of amorphous alloys. The  
438 heating rate plays an important role in the activation energy; for super viscous materials, slow  
439 heating rates increase it, which was beneficial to conserve the amorphous phase in this case,  
440 but the material's densification was reduced. This effect can be compensated with the  
<https://doi.org/10.1016/j.jallcom.2021.160399>.

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441 increment of the uniaxial pressure. In the SPS, the slow heating rates also reduce the  
442 temperature gradient allowing a homogeneous densification process.

443 Materials porosity reduces the corrosion resistance of the materials. However, for metallic  
444 glasses, more advantages have been found in preserving the material's amorphous phase than  
445 reaching higher densities.

446

447

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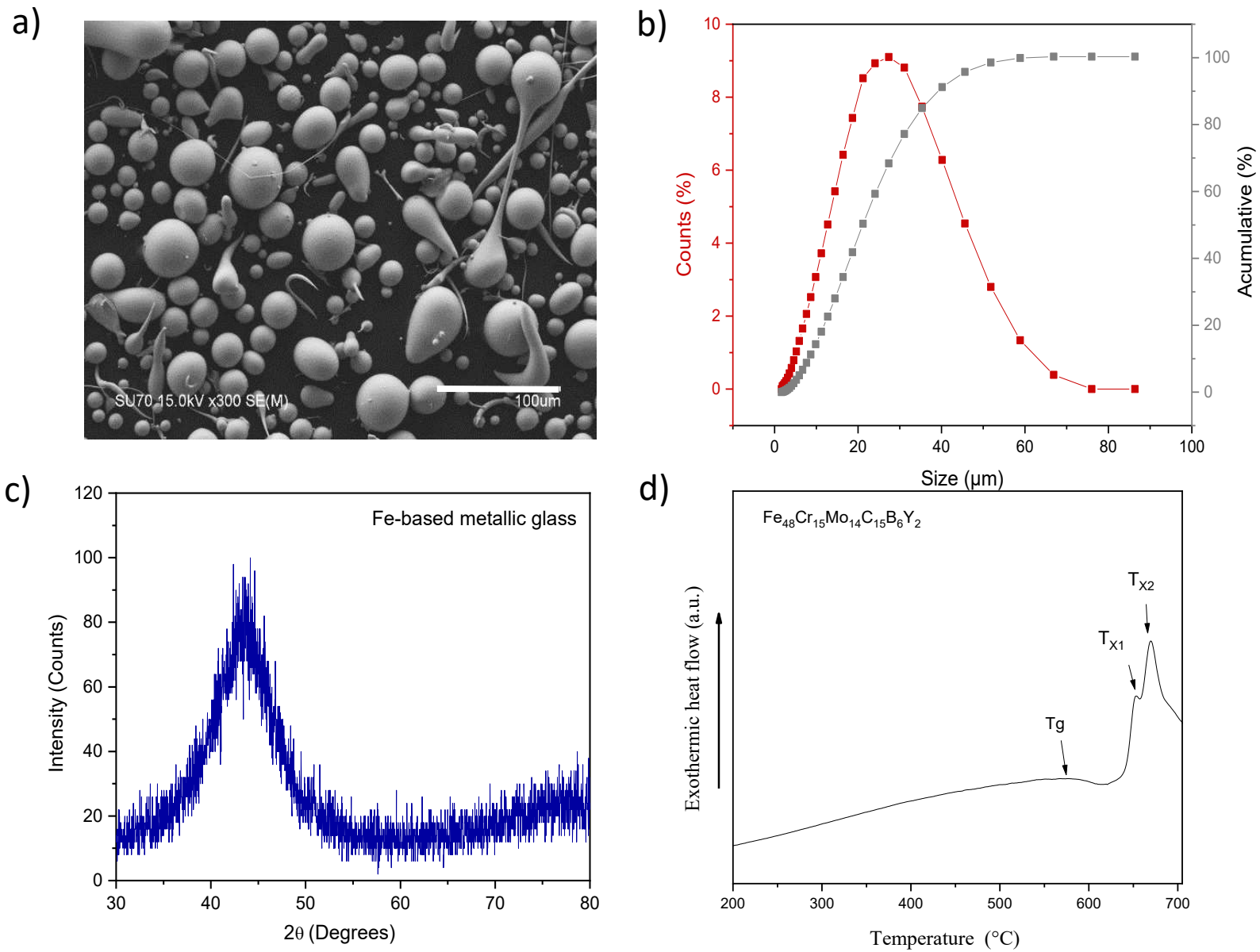


Figure 1. Powder of Fe-base metallic glass, a) SEM observations, b) Size distribution by laser granulometry, c) XR-Diffraction and d) DSC.

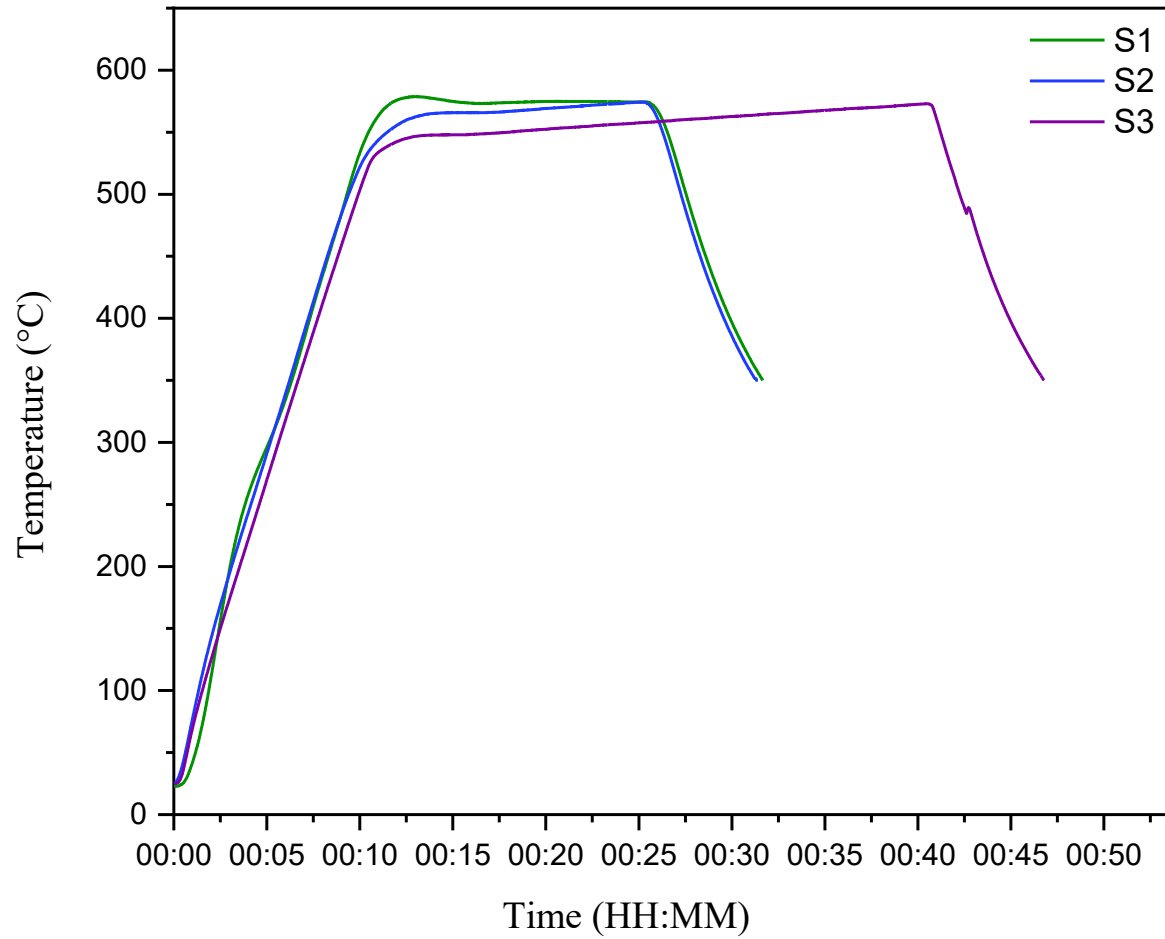


Figure 2. Sintering cycles S1, S2 and S3 with final temperature of 575 °C. Axial pressure 50 MPa.

Sample name	Maximum temperature	Maximum Pressure
S1 – S2 – S3	575 °C	50 MPa
<i>* Differences are in the sintering cycle:</i>		
<i>S1 = Room temperature to 575 °C at 50 °C/min and 15 min of holding time</i>		
<i>S2 = Room temperature to 560 °C at 50 °C/min then to 575 °C at 1 °C/min</i>		
<i>S3 = Room temperature to 545 °C at 50 °C/min then to 575 °C at 1 °C/min</i>		
S4-50	560 °C	50 MPa
S4-100	560 °C	100 MPa
S4-200	560 °C	200 MPa
S4-300	560 °C	300 MPa
S4-400	560 °C	400 MPa
<i>* Identical sintering cycle:</i>		
<i>S4 = Room temperature to 560 °C at 50 °C/min then to 560 °C at 1 °C/min</i>		

Table 1. List of samples and SPS pressure and temperature.

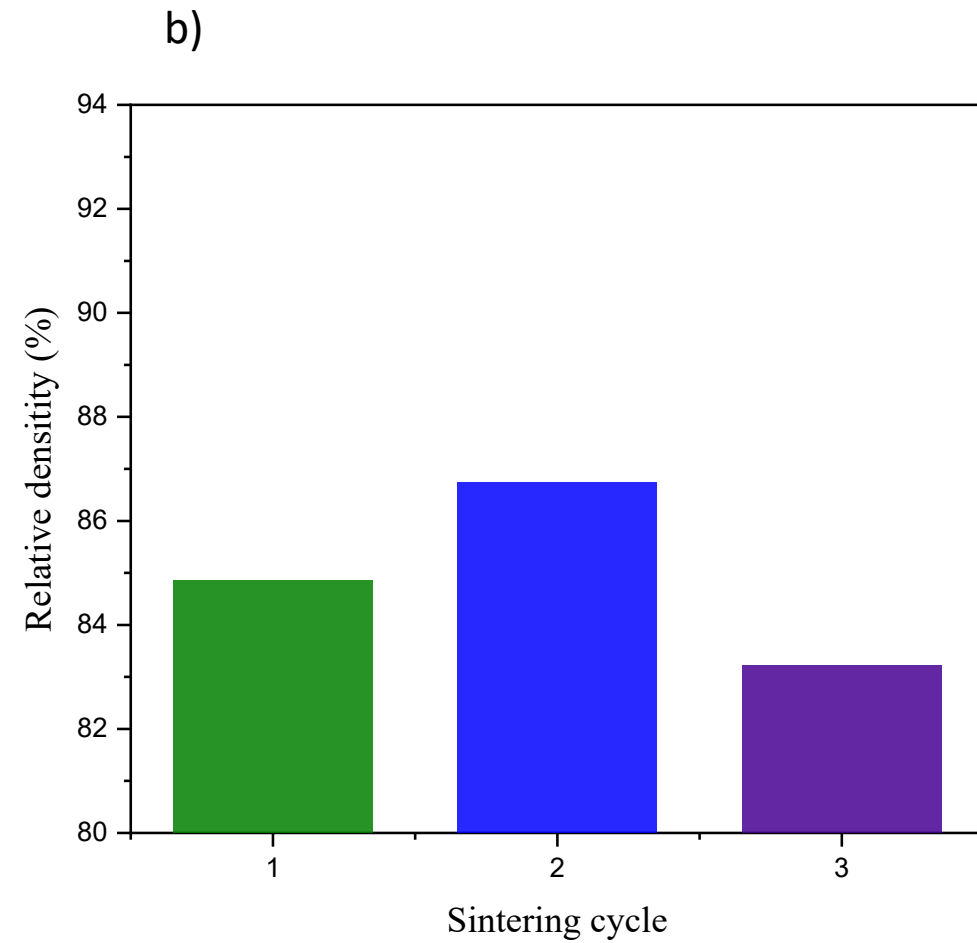
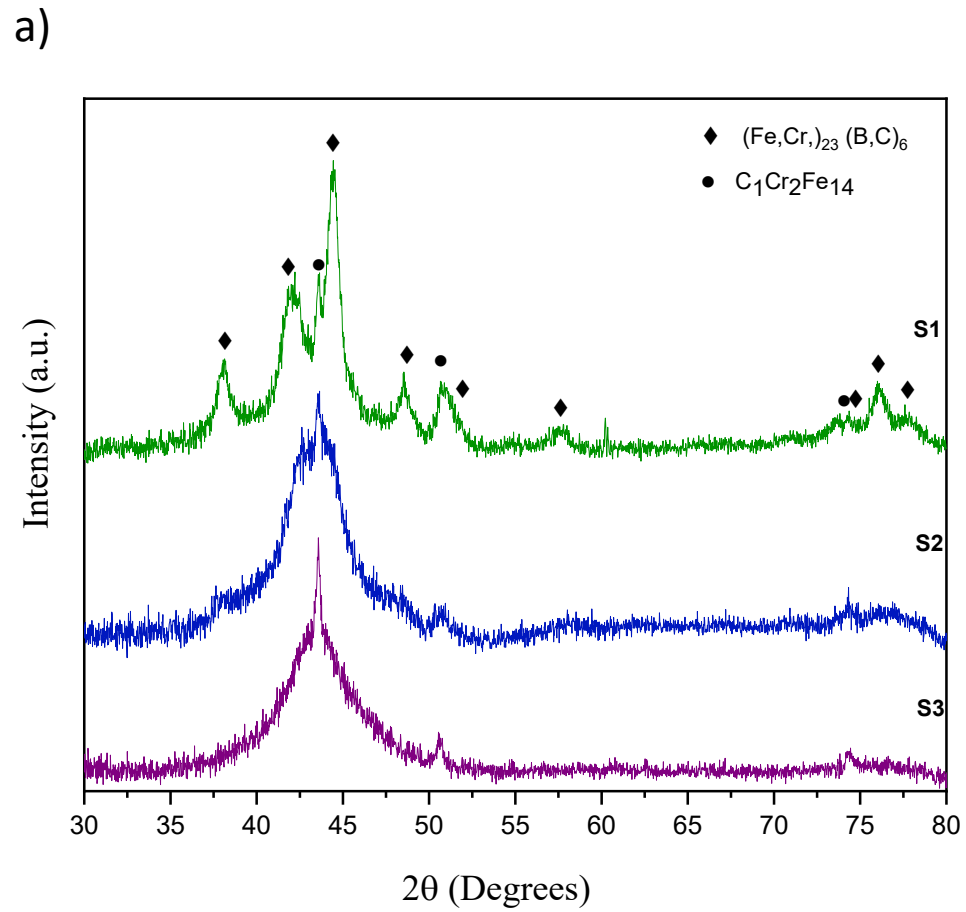


Figure 3. a) X-ray diffraction patterns on BMG and b) density of Fe-base metal glass sintered by S1, S2 and S3 cycles at a maximum temperature of 575 °C (axial pressure 50 MPa).

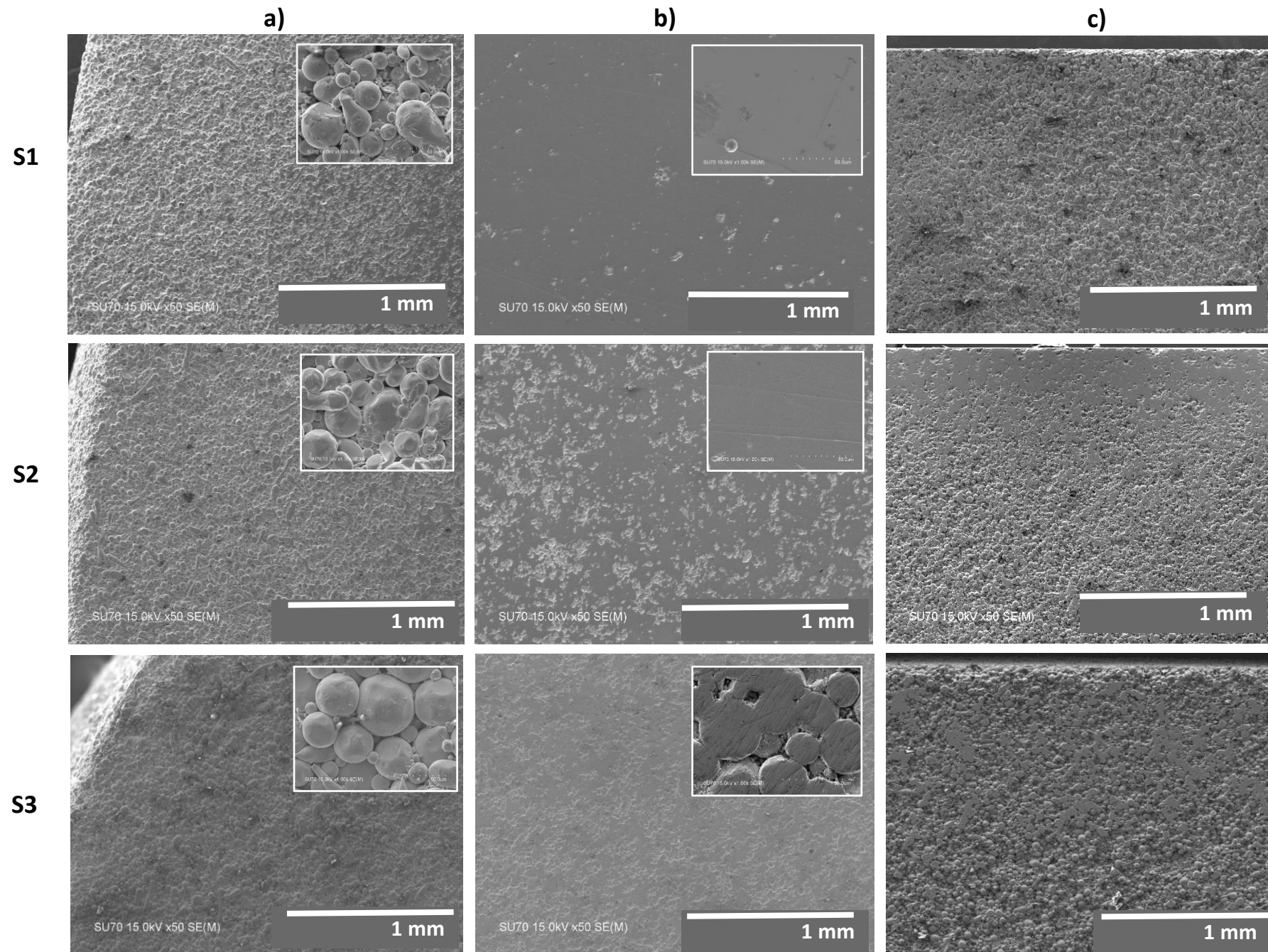


Figure 4. Top surface SEM images of sintered samples (axial pressure 50 MPa) S1, S2, and S3 a) at the edge, b) at the center and c) in cross-section.

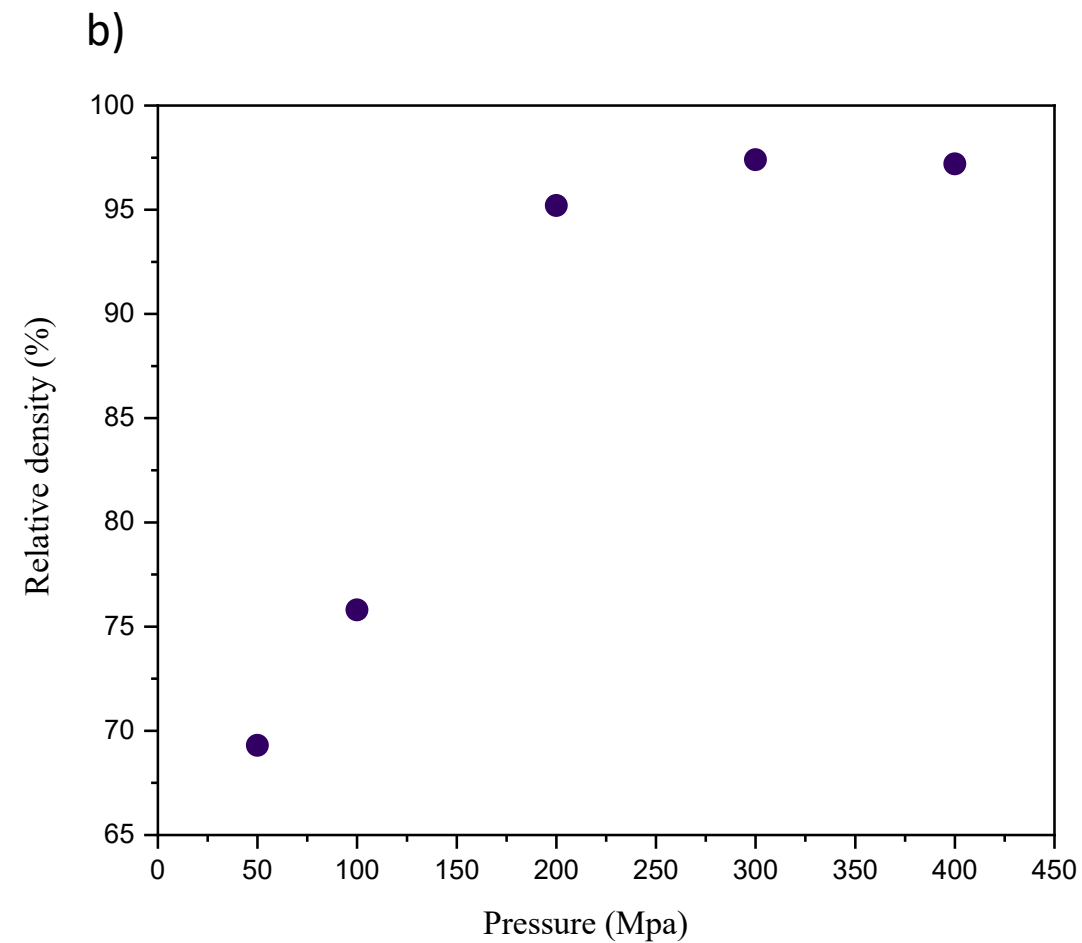
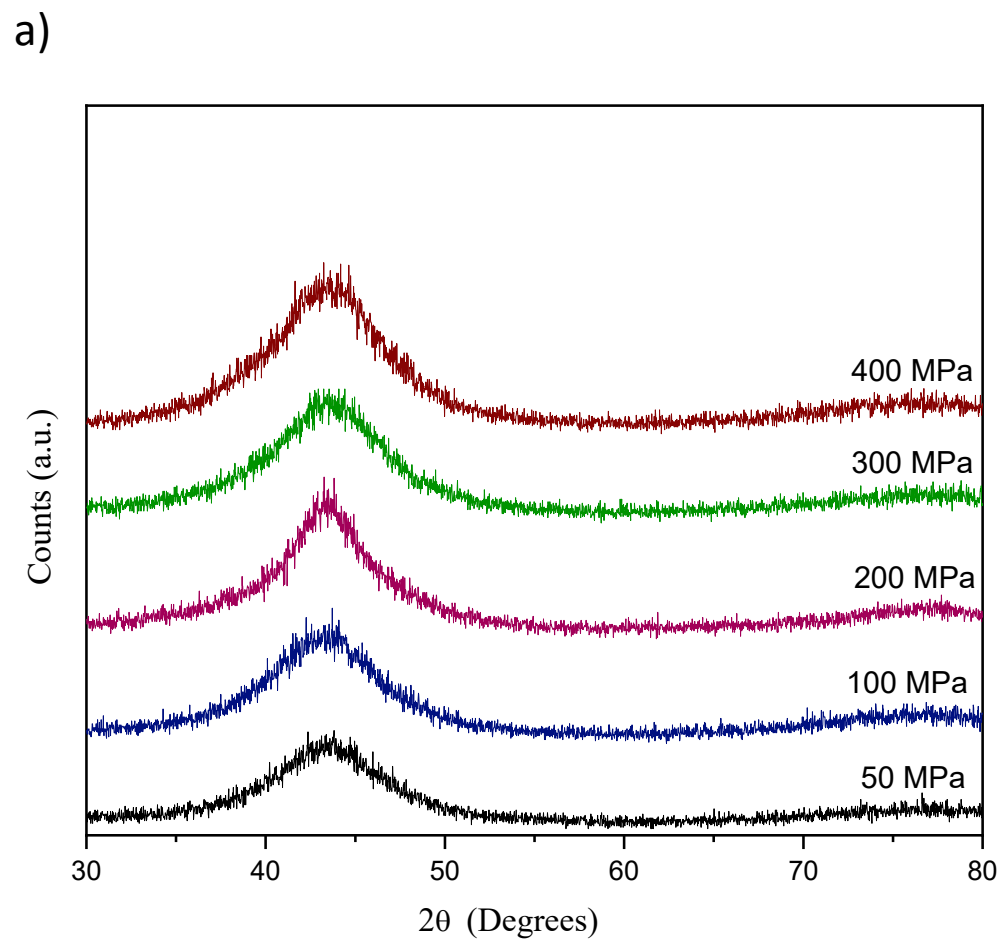


Figure 5. a) Diffractogramas and b) Graph of relative density of Fe-base BMG sintered at 560 °C at different pressures.

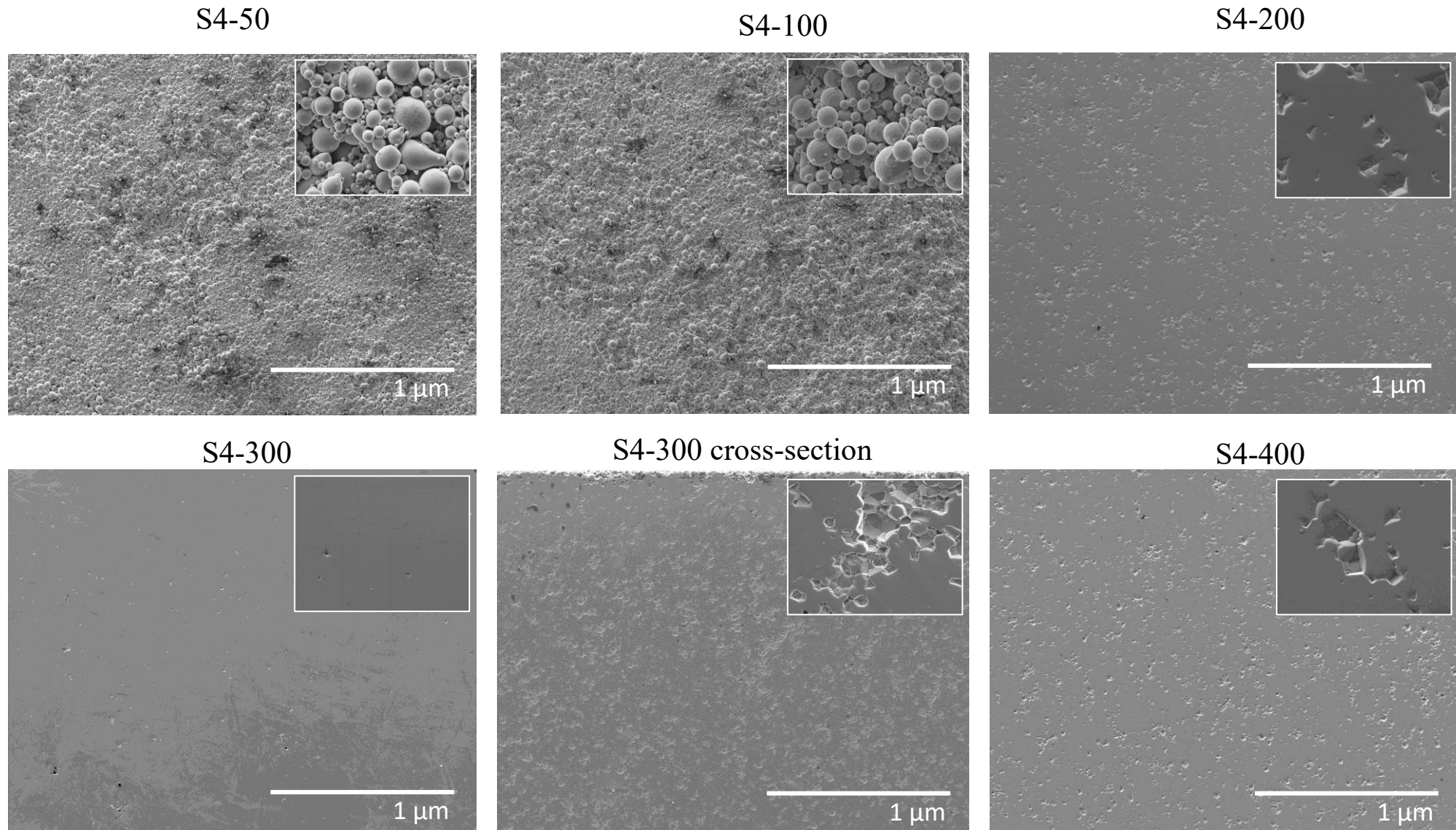


Figure 6. Top surface SEM images at the center of the sintered samples S4 at different uniaxial pressures (MPa) and cross-section of sample at 400 MPa.

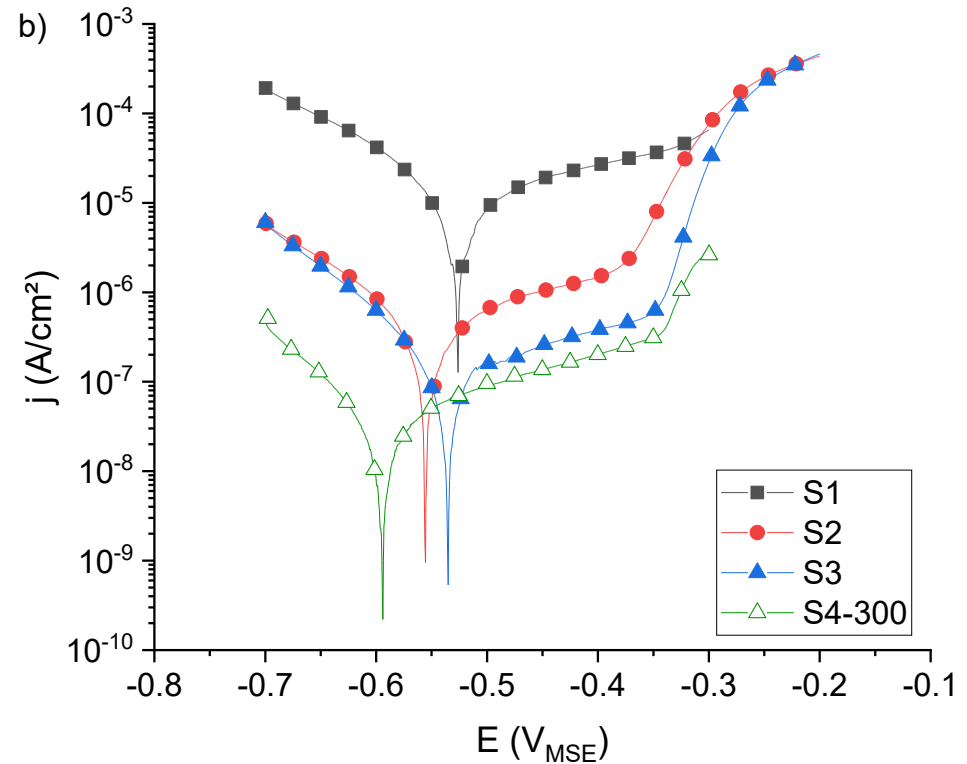
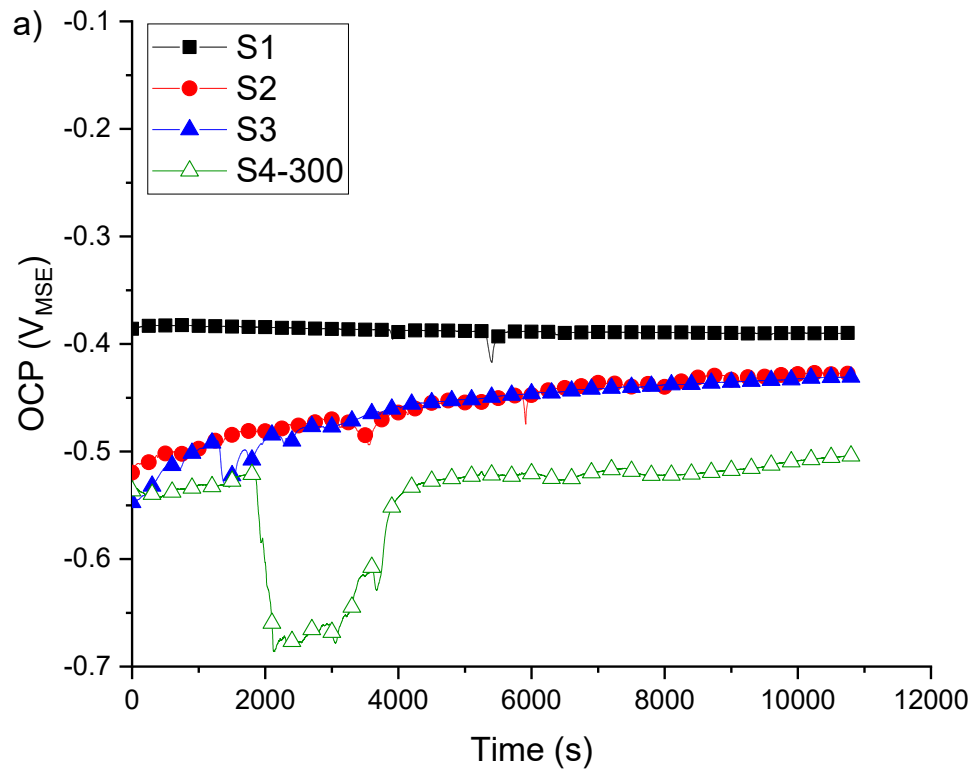


Figure 7 a) Open circuit measurements and b) linear polarization curves on S1, S2, S3, and S4-300 in 10 g/L  $Na_2SO_4$  solution (room temperature, stagnant conditions).

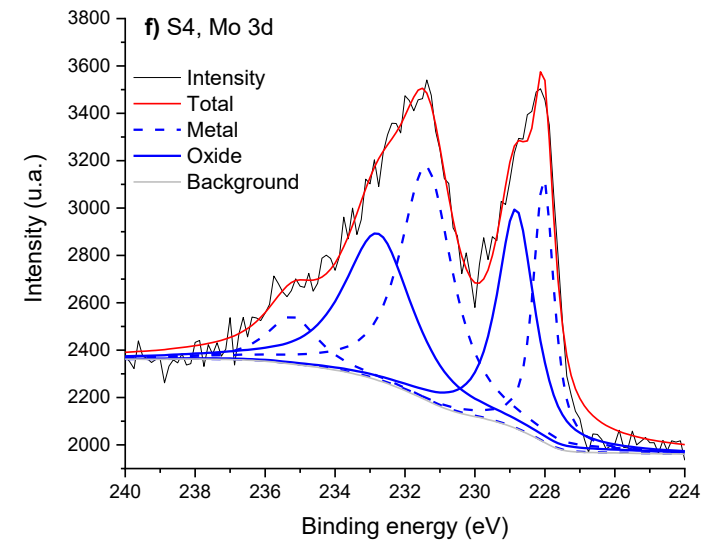
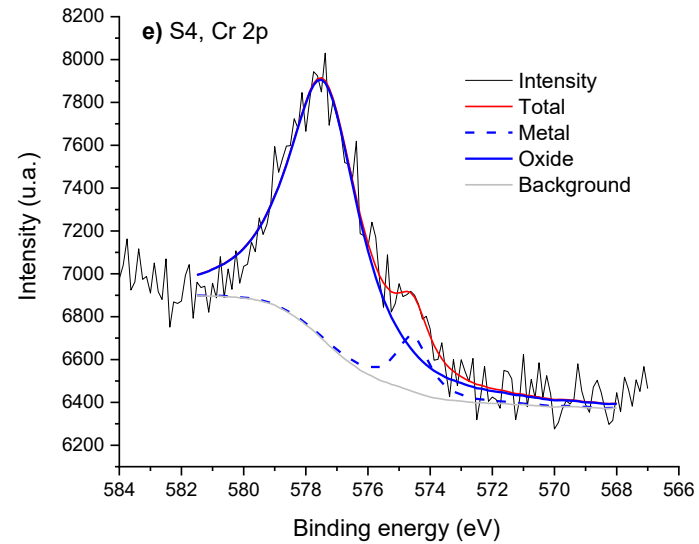
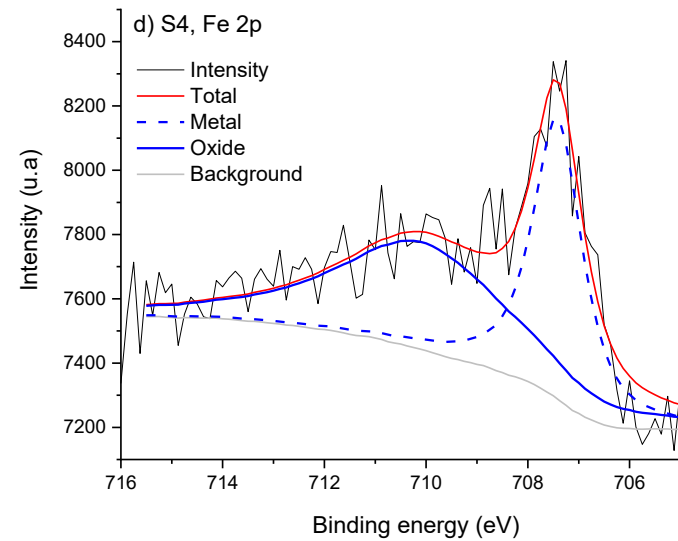
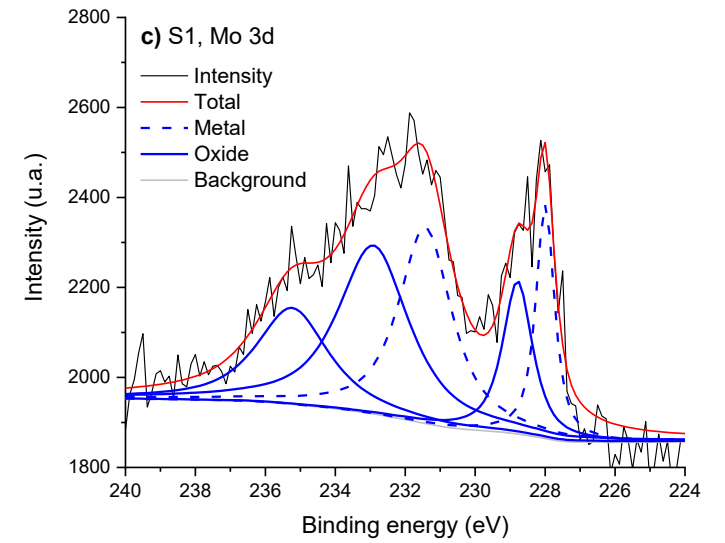
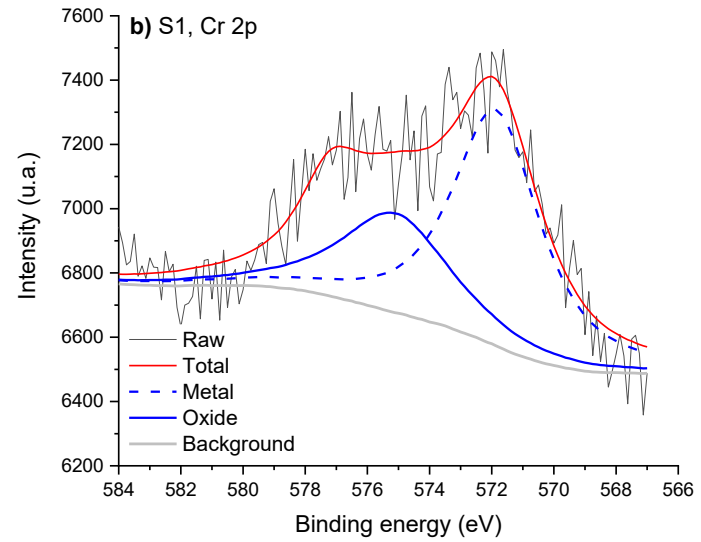
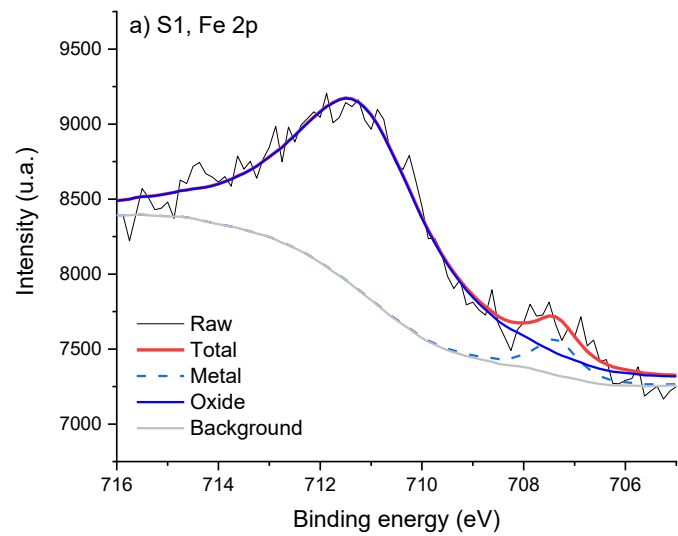


Figure 8. XPS data and fitted Fe 2p, Cr 2p, and Mo 3d spectra for (a-c) S1 and (d-f) S4.

Table 2. Tafel fit on LSV curves for the four samples immersed in a neutral sulfate solution. The equivalent weight was equal to 26.56 g/eq, and the density was taken to 7.9 g/cm<sup>3</sup>.

<b>Samples</b>		<b>S1</b>	<b>S2</b>	<b>S3</b>	<b>S4-300</b>
Crystallinity (XRD)	% ( $\pm 5$ )	70	24	19	<1
Relative density	% ( $\pm 2$ )	85	87	83	97
Roughness	Ra ( $\mu\text{m}$ )	2.7 $\pm$ 5.8	0.52 $\pm$ 0.11	4.10 $\pm$ 0.96	0.55 $\pm$ 0.12
	Rz ( $\mu\text{m}$ )	22.5 $\pm$ 0.5	8.83 $\pm$ 1.00	28.16 $\pm$ 5.12	0.66 $\pm$ 6.02
XPS	$\beta$ ( $\pm 0.15$ )	0.47	0.60	0.72	0.82
<i>LSV curves, Tafel plots</i>					
<b>Samples</b>		<b>S1</b>	<b>S2</b>	<b>S3</b>	<b>S4-300</b>
$E_{\text{corr}}$	$V_{\text{MSE}}$	-0.527	-0.555	-0.535	-0.594
$J_{\text{corr}}$	$\times 10^{-6}$ A/cm <sup>2</sup>	10.9	0.403	0.112	0.003
Tafel coeff. $\beta_a$	mV/decade	352	313	247	220
Tafel coeff. $\beta_c$	mV/decade	129	133	84	96
Corrosion rate	$\times 10^{-3}$ mmpy	82.0	4.80	0.98	0.31
<i>EIS Fits (<math>\chi^2/ Z  &lt; 0.05</math>)</i>					
<b>Samples</b>		<b>S1</b>	<b>S2</b>	<b>S3</b>	<b>S4-300</b>
		$R_e + Q_{\text{sc}}/(R_{\text{ct}} + W)$	$R_e + Q_{\text{sc}}/(R_{\text{ct}})$		
$R_e$	$\Omega \text{ cm}^2$	129	65	71	52
$Q_{\text{sc}}$	$F s^{(n-1)} \text{ cm}^{-2}$	$700 \times 10^{-6}$	$97 \times 10^{-6}$	$67 \times 10^{-6}$	$39 \times 10^{-6}$
$n$	u.a.	0.60	0.80	0.82	0.78
$R_t$	$\Omega \text{ cm}^2$	95	$88 \times 10^3$	$341 \times 10^3$	$22 \times 10^6$
$\sigma_1$	$\Omega s^{1/2} \text{ cm}^2$	$1.06 \times 10^3$	--	--	--
$C$	$F \text{ cm}^{-2}$	$23 \times 10^{-3}$	$166 \times 10^{-6}$	$133 \times 10^{-6}$	$262 \times 10^{-6}$

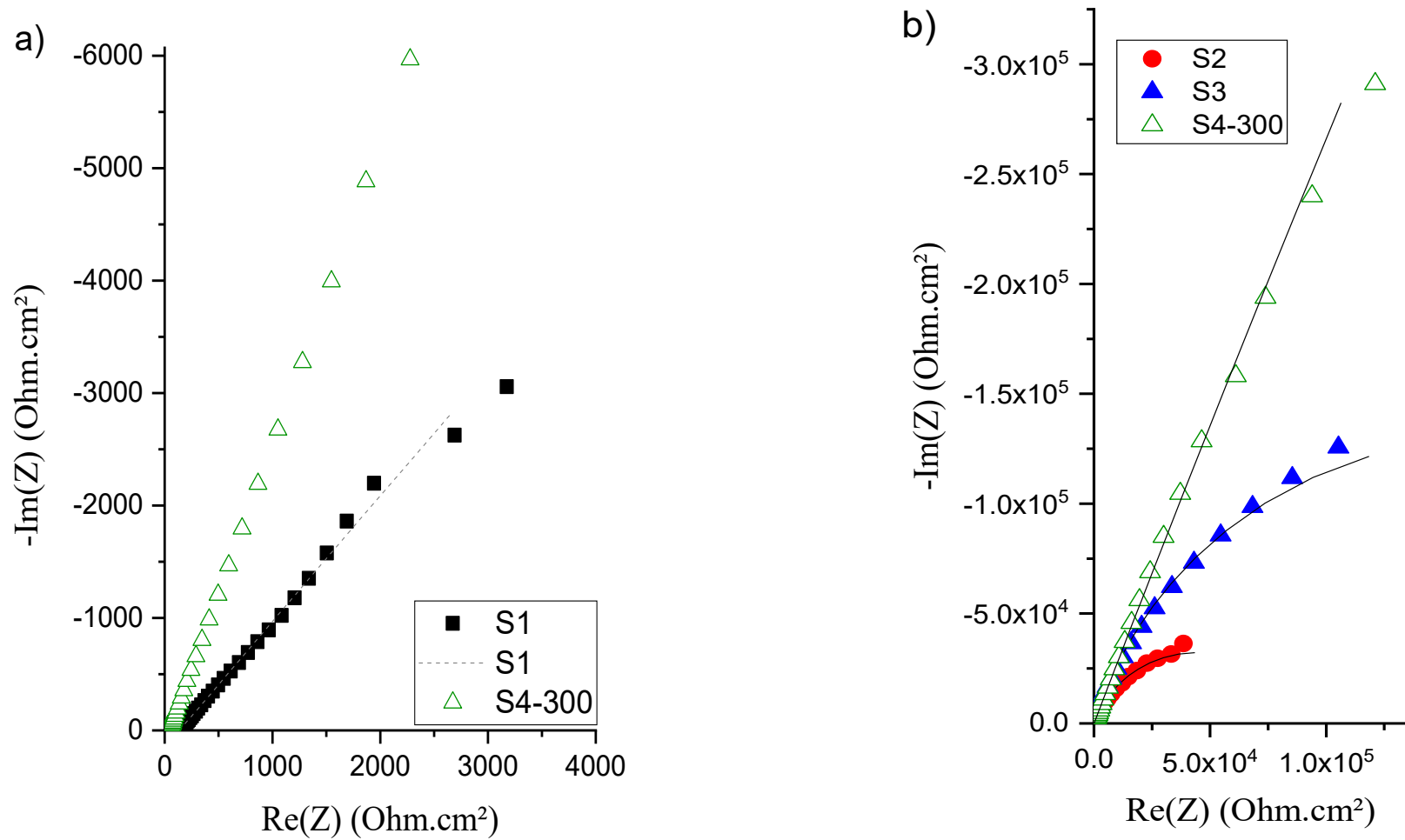


Figure 9. Nyquist diagrams on four samples immersed in an aerated, stagnant sulfate solution. a) zoom for S1 sample (high crystallinity ratio) and b) comparison between samples with low crystallinity ratio. The dash lines are the results of the EEC fits.