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Evaluation of the Corrosion Resistance of Watch Links from 316L and 904L Austenitic Stainless Steels Obtained by the Metal Injection Molding (MIM) Technique Intended to Be in Contact with Human Skin

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Abstract: Watchmaking manufacturers obtain their bracelet links from machining drawn metal profiles. But, today, there is another process that represents an alternative to manufacture them: metal injection molding using metal powders (MIM technology). This process is less expensive than the machining of drawn metal profiles. The aim of this study was to evaluate the corrosion behavior and the nickel cation release of two stainless steel alloys: 316L MIM and 904L MIM. The general corrosion behavior was evaluated by the rotating electrode technique; the galvanic corrosion measurements were conducted with a 316L AISI bulk coupling partner. The pitting corrosion behavior was evaluated in FeCl₃ 0.5 M media (according to ASTM G48-11). For comparison, a complementary study was conducted on 316L and 904L bulk alloys. The Ni cation release tests were conducted on 316L and 904L MIM and bulk samples according to EN 1811. Different electrochemical parameters were measured and calculated (open circuit potential, polarization resistance, corrosion current and Tafel slopes, coulometric analysis). Generally, if MIM steels are compared with conventional steels, their corrosion resistance behavior is inferior. In the couplings studied, the galvanic currents generated are very important. The shape of the curves also reveals the presence of localized corrosion phenomena. According to tests in ferric chloride, MIM steels were noted to have inferior behavior compared to conventional steels. MIM type 904L steels are comparable in behavior to conventional type 316L steels. The quantities of nickel released according to EN 1811 were very significant (2 mg cm⁻² week⁻¹ up to 24 mg cm⁻² week⁻¹) and did not meet the requirements of the European directive (0.5 µg cm⁻² week⁻¹). In conclusion, conventional steels studied under the same experimental conditions revealed a better behavior compared to MIM steels independently of the phenomenological parameters chosen.

Keywords: metal injection molding; MIM; 316L steel; 904L steel; generalized corrosion; galvanic corrosion; pitting corrosion; nickel release; allergy of nickel



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1. Introduction

Powder metallurgy is the process of obtaining components and objects from metals and ceramics powders. The powder materials are mixed, pressed into a desired shape and then heated in a controlled atmosphere to bond the contact surfaces of the particles and to achieve the geometric shape of the desired object. Thus, the manufacturing techniques generally adhere to the following steps: *powder synthesis* (atomization, precipitation, decomposition), *powder preparation/development of feedstock* (grinding, agglomeration, mixing with plastic binder, granulation), *formatting* (ceramic or metal injection molding—CIM/MIM, extrusion, pressing/compaction, pouring, sol-gel, infiltration) and *densification* (sintering, hot pressing, hot isostatic pressing (HIP), gas pressure sintering (GPS)) [1]. MIM is therefore a shaping process, as shown in Figure 1.

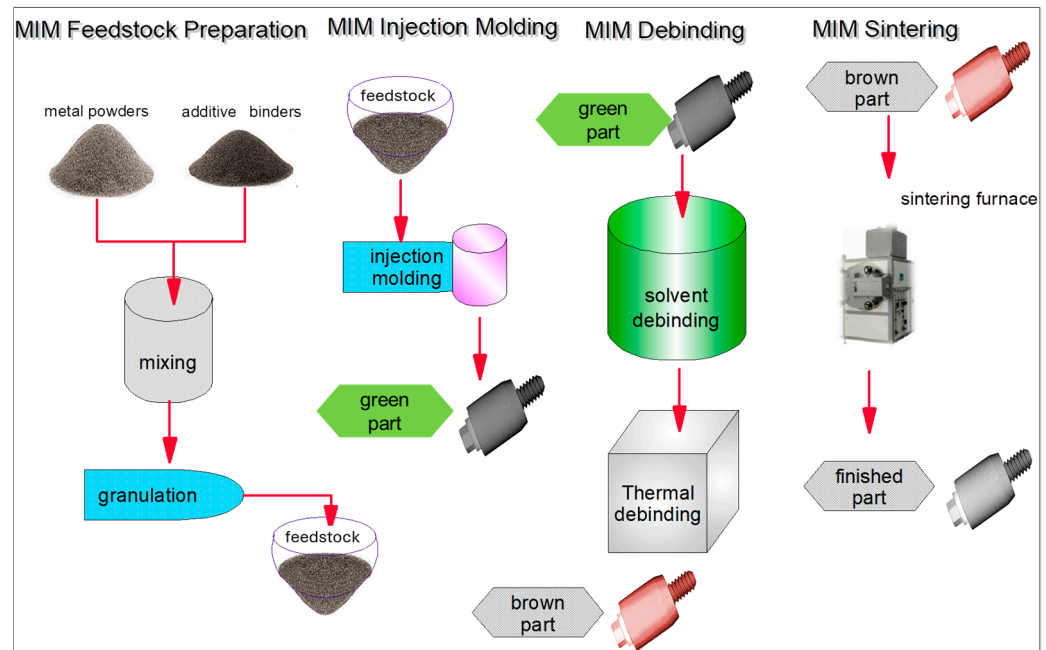


Figure 1. MIM process steps.

Powder synthesis. The properties of articles obtained by powder metallurgy are highly dependent on different powder characteristics (chemistry and purity, particle size, size distribution, particle shape and particle surface texture). Several processes can be used, and each of these give distinct properties and characteristics to the powder and therefore to the final product:

- *Gas atomization*, where jets of high-pressure gas (usually nitrogen, argon or helium) strike a stream of liquid metal as they emerge through the nozzle;
- *Liquid under pressure* (usually water) can replace gas under pressure by transforming it in an atomization process with water;
- In *another system*, an electric arc encroaches on a rapidly rotating electrode. The centrifugal force causes the molten metal droplets to fly from the surface of the electrode and freeze in flight.

Water and gas atomization processes are generally used to obtain powders with a spherical geometry, especially from stainless steels such as 304L, 316L and 904L. Regarding the size, powders manufactured by chemical techniques generally have smaller dimensions (0.2–5 µm) than those obtained by water or gas atomization (4–40 µm) [2].

Feedstock elaboration. This step consists of mixing a powder and a polymer-based binder. The mixture is generally created using mixers and/or extruders at a high shear rate to ensure good homogeneity.

The binder must be thermally resistant to the mixing, granulation and shaping stages without degrading, and then it must be able to be disposed relatively easily in the debinding stage [3]. Generally, multi-component systems based on *thermoplastics* (polyolefins) ensure the flow during the injection phase and the strength of the component not only after injection but as long as possible during the debinding stage. *Waxes* are also widely used to reduce the viscosity of the binder to promote injectability.

The ratio between the powder and the binder is also a very important parameter. The loading rate, T_c , is defined as the ratio of the powder volume to the total volume of the powder and binder. A higher loading rate causes a very high viscosity, which makes the injection stage difficult. In addition, the presence of air bubbles in the feedstock mass can be the cause of the appearance of defects such as cracks during the debinding stage [4]. A lower loading rate can lead to significant inhomogeneities in the brown part as well as to a sagging of the brown part during the debinding stage. At a loading rate of 50%–65% by

volume, the viscosity is still optimal for good injection, and the powder grains' contact is sufficient to maintain the shape of the brown part during the entire process.

Formatting: Injection. The injection cycle is as follows. The material placed in the hopper of the injection press arrives in the sheath, and then it is conveyed by an endless screw and heated by thermal input. The screw stops rotating, and the mold is then filled under pressure. The part is then ejected when the mixture has cooled sufficiently. At this stage of the process, the injected part is called the "injection raw" or "green part", and it does not have the same dimensions as the final one due to the shrinkage phenomenon, which occurs during the sintering stage. Oversizing must be determined precisely to respect the tolerances imposed on the final part.

The main controlled molding parameters are as follows: the material temperature, the mold temperature, the injection pressure and the speed [5]. The material temperature modifies the feedstock viscosity, which decreases as the temperature increases. The temperature of the mold determines the flow of the feedstock. The injection pressure influences the internal tensions, shrinkage and dimensional stability of the final parts. As the pressure is applied longer and more consistently, the part becomes more stable during the entire process.

The segregation phenomenon between the binder and the powder is difficult to identify after injection and has dramatic consequences on the integrity of the sintered parts since it causes anisotropic shrinkage and therefore very significant deformations. It is favored by the use of binders that reveal low viscosities (such as waxes) [6].

Debinding. This stage consists of removing organic binders from the feedstock once the part has been injected. There are two distinct debinding stages. In the first stage, debinding is carried out to open the channels (capillaries) from the heart of the part to its periphery. A quantity of the binder remains, and its role is to maintain a certain mechanical resistance to the part, allowing it to be manipulated. In the second stage, which is always the thermal stage (pre-sintering), it is necessary to eliminate the rest of the organic binder.

Depending on the feedstock used, the binder rate can vary between 35 and 50% vol. This corresponds to a linear shrinkage of 13 to 21% (reduction between injected and sintered geometric dimensions X, Y, Z). This is a difficult step to control despite requiring the fewest adjustments to make.

Debinding is essential to avoiding causing physical (cracking) or chemical (carburizing) damage to the part. A significant quantity of defects that appear after sintering is generated by inadequate debinding. Its parameters (temperature, atmosphere, etc.) depend not only on the binder type but also on the powder (metallic or ceramic). There is therefore a modification of the chemical-physical, mechanical and biological properties, which no longer correspond to the demanding requirements (special for the metal or a ceramic objects that are in contact with living tissue) [7–9].

Another problem that poses great difficulties in this stage is the pollution of ovens by the presence of carbon residues that come into contact with the pre-sintered parts.

Densification: Sintering. This is the last step of the MIM process, where the part must be consolidated, and the cohesion and the typical microstructure of the final material must be obtained. Sintering is accompanied by controlled shrinkage.

The principle of sintering is based on atomic diffusion; metals or ceramics are welded by a diffusion mechanism at the sintering temperature [10]. There are two forms of sintering: in the absence of a liquid phase and in the presence of a liquid phase [11]. Sintering operations have three stages and must be carried out in oxygen-free conditions under a vacuum or a protective atmosphere:

A. The first temperature stage is designed to burn the air and volatilize and remove lubricants or binders that could interfere with the proper bonding of the metal particles. When the compacts contain appreciable amounts of volatile materials, their removal can create porosity and additional permeability in the pressed form.

B. The second stage, or high temperature, is where the desired solid-state diffusion and bonding between the powder particles take place. As the material seeks to decrease its surface energy, the atoms move toward the contact points between the particles. This is sintering in the absence of a liquid phase. In this stage, other phenomena must also be controlled, such as deoxidation phenomena, control of the carbon level and the evaporation of certain elements.

C. The third stage is a period of cooling the parts while keeping them in a controlled atmosphere. This procedure serves to prevent oxidation that could occur during direct release into the air and rapid cooling.

With current technologies, a new concept has been developed: the work pieces are placed in a pressurized oven that can be sintered under a vacuum for sufficient time to seal the surface and eliminate any internal porosity. This process is called hot isostatic pressing (HIP) [12].

Stainless steels. Powder metallurgy technology has undergone a strong evolution, particularly MIM, in the manufacturing of metal parts with geometric complexity. These items can be produced in quantities of thousands in a relatively short period of time and at very competitive costs. They affect a very wide range of applications, such as the automotive industry, aerospace, medical devices, consumer products (watches, toys, jewelry, household items), etc. Currently, through knowledge and know-how, a multitude of alloys can be used (steels, stainless steels, nickel-based alloys, super alloys, titanium-based alloys [13–16], tantalum titanium, niobium alloys) [17–33]. Very interesting applications are found in dental medicine [34].

Despite being called stainless steels, they are very sensitive to corrosion localized forms, namely pitting, crevices and intergranular corrosion. The formation of an oxide layer on the metal surface (natural passivation) provides it some protection in different chemical environments.

Metals undergo a change described as a variation in valence and electron density in equilibrium with possible ionic states. Passivity is the result of the layer's formation on the metal surface of a low electrical conductivity. Various theories have been developed to explain the formation of the passive layer. One of the most generally accepted is the formation of a stable OH^- (oxy-hydroxide hydrate) film in the range of a few millivolts around the redox potential, E_{cor} (mixed corrosion potential). The thickness of this film is between 10 and 100 Å. Passivity, in general, is a kinetic inhibition of the capacity of metals and alloys to react with the medium in contact with their surface. Passivity results in the formation of an ultra-thin film, which is compact, dense and free of porosities and which uniformly covers the metal surface. Today, it is known that the stationary state of these films are layers of solid oxides and not mono-molecular adsorption layers [34].

The protective oxide film can be subjected to attack followed by localized degradation, which leads to pitting and crevice corrosion morphologies of the steel. Sintered stainless steels, superalloys and nickel-based alloys also undergo corrosion through the occasional destruction of their oxide layer formed on the surface. But in sintered materials, inherent pores and crevices are part of the material. Depending on their dimensions, these pores can act as initiation markers for pitting and crevice degradation of the materials.

A large part of the bibliographic resources on the corrosion of PM alloys reports immersion tests in chloride and salt spray environments [35–38]. Test results can provide useful information for some systems, but they are often not sufficiently described to evaluate similar alloys. In addition, they do not provide information on the nature or mechanisms of the corrosion of PM alloys.

In fact, mechanisms of degradation in an artificial environment, such as salt spray, are often very different from those of a natural environment. These tests can be considered as screening tests.

Also, tests in orthodontics involving the galvanic coupling of conventional and metal injection molded (MIM) brackets with various nickel–titanium or copper–nickel–titanium wires are conducted by immersion in lactic acid [39,40].

Corrosion resistance studies of CoCrMo MIM alloys in the manufacturing of orthopedic prostheses have also been reported [41,42]. In watch clothing, MIM technology is commonly used to obtain links for bracelets. MIM links are made of 316L and 904L steels. Nickel is found in the composition of these alloys.

The role of nickel in the biological response to alloys used in medical devices is of immense significance regarding toxicology and biological performance. There is now a tendency to take nickel out of alloys for medical applications. However, this needs careful evaluation, since no compromise is acceptable regarding the mechanical properties, corrosion resistance or any other harmful consequences due to nickel substitution [43].

Nickel allergy is the most widespread of all contact allergies. In the general population, the prevalence is 10%–15% of adult females and 1%–3% of adult males in Europe who are allergic to nickel [43,44]. Of nickel-sensitive people in the general population, 30% develop hand eczema.

Nickel is the object of two European directives: 94/27/CE and 2004/96/CE. Today, it is found in Annex XVII of the REACH regulation with restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles. It shall not be used [45] (a) in any post assemblies that are inserted into pierced ears and other pierced parts of the human body unless the rate of nickel release from such post assemblies is less than $0.2 \mu\text{g}/\text{cm}^2/\text{week}$ (migration limit); or (b) in articles intended to come into direct and prolonged contact with the skin, such as earrings, necklaces, bracelets and chains, anklets, finger rings, wristwatch cases, watch straps and tighteners, rivet buttons, tighteners, rivets, zippers and metal marks, when these are used in garments, if the rate of nickel release from the parts of these articles coming into direct and prolonged contact with the skin is greater than $0.5 \mu\text{g}/\text{cm}^2/\text{week}$ [45].

Thus, in the manufacture of bracelets and other articles specific to watch clothing, there is a trend of replacing these steel grades with nickel-free austenitic steels. Attempts are being made today to transfer these steel grades to MIM technology [34,46–55].

The purpose of the current study was to study the potential of using watch bracelet links obtained by MIM processes intended to be in contact with the skin. This was a request of a Swiss watchmaking group. The corrosion behavior of several stainless steels obtained by MIM and MIM + HIP were evaluated by different electrochemical techniques. Common stainless steels were also tested in the same media. In the manufacture of bracelets in link and pin assembly, galvanic currents can be generated by the presence of sweat or other aqueous electrolytes (sea water, swimming pool water, rain or condensation of atmospheric humidity). For this reason, direct measurements of the galvanic couplings between MIM alloys and common steels were carried out.

The pitting potential of these alloys was also evaluated by applying the ASTM G48-11 standard for ferric chloride [56].

2. Materials and Methods

2.1. Materials

Ten MIM stainless steels were investigated: 316L (#1 to #6) from one supplier and 904L P (#7 and #8) and 316L A (#9 and #10) from a second supplier, as shown in Table 1. These materials were obtained according to various technological manufacturing conditions:

- Milling $\times$ 1 Time: This is a feedstock in which the metal powder is obtained by grinding once;
- Milling $\times$ 2 Times: This is a feedstock where the metal powder used is obtained by grinding twice.

Table 1. Sample identification.

Code	Material Powder	State of the Feedstock	Cycle	Process
#1	316L	Green	Long	Sintering and HIP
#2	316L	Green	Long	Fritting and HIP
#3	316L	Milling $\times$ 1 Time	Short	Sintering
#4	316L	Milling $\times$ 1 Time	Short	Sintering and HIP
#5	316L	Green	Short	Sintering
#6	316L	Green	Short	Sintering and HIP
#7	904L	Green	Short	Sintering and HIP
#8	904L	Milling $\times$ 1 Time	Short	Sintering and HIP
#9	316L	Milling $\times$ 2 Times	Short	Sintering
#10	316L	Milling $\times$ 1 Time	Long	Sintering

For a better understanding of sampling and manufacturing processes, we reorganized the samples according to a diagram that takes into account the various technological parameters chosen by the manufacturer (Figure 2).

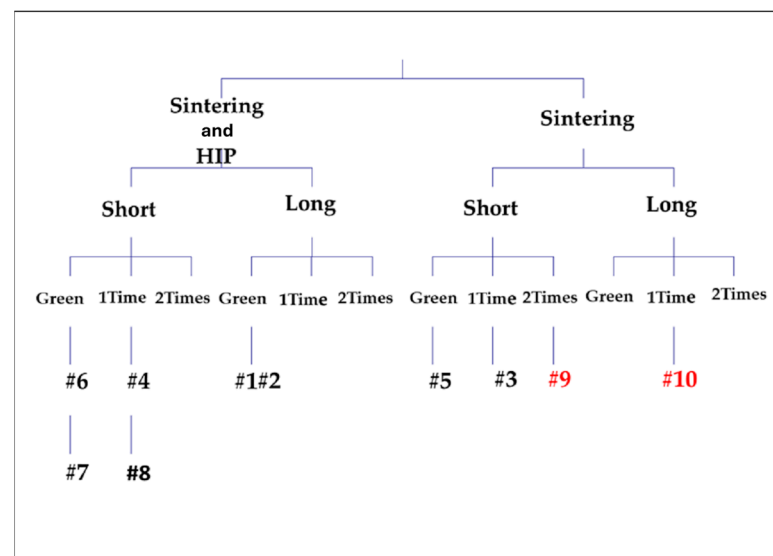


Figure 2. Diagram of test samples according to technical manufacturing parameters. In black the samples provided by the first supplier and in red the samples provided by the second supplier.

The samples prepared by the supplier were discs with diameters of 10 mm. The test surfaces were “mirror” polished with diamond paste with a particle size of 0.1 μm . The samples were embedded in a self-curing methyl methacrylate resin and then polished with SiC paper and finally with diamond spray (6/3/1 microns). Electrolytic etching was carried out in a bath of 100 mL of H_2O , 10 mL of HCl and 5 g of Cr(VI)-oxide for 5 s under 0.4 V and 0.3 A. The alloy microstructures were observed using a metallographic microscope (Polyvar Met, Reichert-Jung, Vienna, Austria). A scanning electron microscope (Sigma, Zeiss, Jena, Germany) and an Oxford X-MAX EDX Instrument for microanalysis were also used. The analyzed samples were covered with a gold flash.

2.2. Evaluation of Corrosion Behavior Using Electrochemical Techniques

Generalized corrosion. The use of the rotating electrode technique allows the control of mass transfer phenomena according to Levich’s theory (1942) [57–60]. An expression for the Nernst diffusion layer specific to the rotating electrode is obtained; in other words, each

dissolved species that reacts in the electrochemical system has its own Nernst diffusion layer. Another factor that significantly influences the corrosion process is the amount of oxygen dissolved in the electrolyte.

In these tests, the medium was deaerated with argon, which allowed measuring the quantity of the dissolved oxygen during the test at 0.2 mg/L. The measurement system was managed by a modified EG&G Par 273A potentiostat with a background noise of 1pA. The corrosion cell was a glass cell specific for the rotating electrode technique. The counter electrode was made of platinum, and the reference electrode was a saturated calomel electrode (SCE). The electrochemical cell was protected by a Faraday cage. The measurements were made in a laminar regime (the criterion of $Re = 3200$) with a limiting current of $i_L = 56$ mA and a rotation speed of 300 rpm to control mass transfer phenomena (mainly the diffusion phenomenon). A presentation of the rotating electrode technique is shown in Figure 3. Figure 4 presents the electrochemical assembly diagram of the rotating electrode.

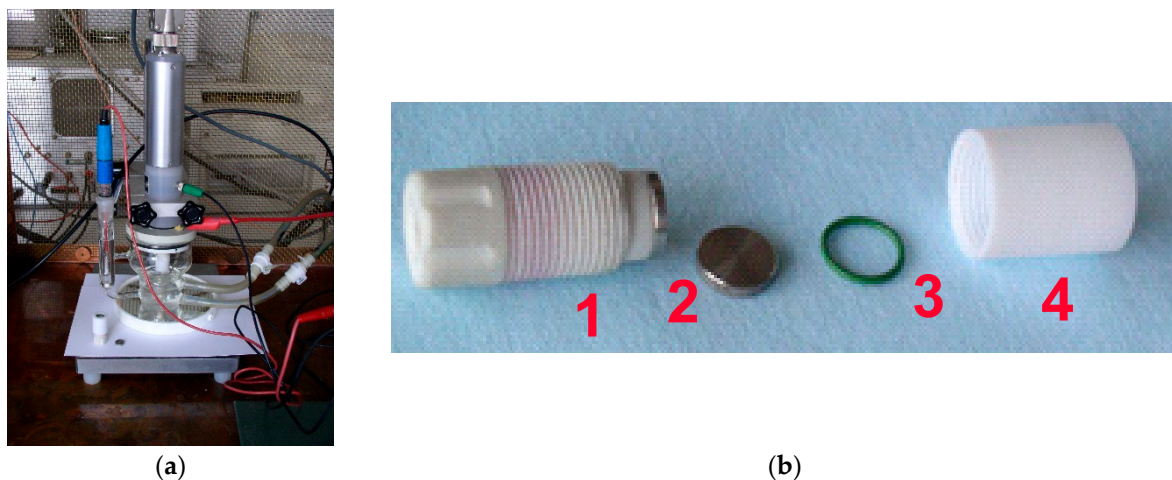


Figure 3. Rotating electrode technique. (a) Rotating electrode cell used in the tests; (b) Electrode composition; 1. PTFE electrode holder; 2. Sample to be tested; 3. Collar; 4. PTFE electrode holding head.

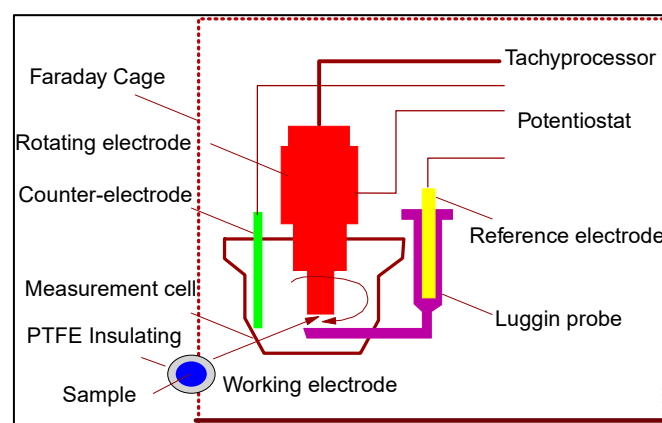


Figure 4. Electrochemical assembly diagram of the rotating electrode.

The electrochemical evaluation of generalized corrosion was carried out using different ASTM standards, such as ASTM G3-14, ASTM G5-14 and ASTM G59-97 [61–63].

The electrochemical parameters measured were as follows:

- The open circuit potential recorded during immersion in the deaerated electrolyte with Ar for 16 h;

- The polarization resistance (R_p) calculated from the plotted polarization curve (± 20 mV);
- The Tafel slopes and the corrosion current (i_{corr}) calculated from the polarization curve (± 150 mV);
- The coulometric analysis by zone drawing the overall polarization curve (-1000 mV to $+1000$ mV).

Evaluation of galvanic corrosion by direct coupling measurements. Link–pin assemblies are ideal cases for the formation of galvanic cells, where an electric potential difference of 50 to 100 mV can be measured. It has a release of cations toward the skin. This is the typical case of nickel release, which today is regulated by REACH Annex XVII [44].

There is also the aspect of the cathode–anode ratio. The surfaces of the MIM steel link are significantly larger than the surfaces of the pins (rods). Constructions with large cathode surfaces and small anodic surfaces are very dangerous. The galvanic cell delivers a strong anodic current that leads to rapid degradation of the anodic part by corrosion mechanisms in crevices or pitting. This is probably the type of corrosion most frequently found in bracelet constructions. The most direct procedure for galvanic cell measurements involves immersing two dissimilar metals in an electrolyte and electrically connecting them to measure the galvanic potential and current (i_{galv} , E_{galv}) using a zero-resistance ammeter. This technique is very accurate for time-dependent polarization but is expensive and time-consuming. In general, couplings are measured for 3 to 4 days to obtain reliable information. Individual samples can be weighed before and after testing to determine the corrosion rate as a function of potential and thus make corrections if necessary using Faraday’s Law.

The samples were mounted on PTFE sample holders. The measuring cell was made of glass, and the measuring electrodes were positioned horizontally opposite each other. The reference electrode was a saturated calomel electrode (ECS). The galvanic current as a function of the coupling time was measured by an EG&G PAR model 273A potentiostat with the electronic modifications indicated by the manufacturer of the device. These modifications made it possible to measure galvanic coupling currents of around 100 pA. The electrochemical assembly is shown schematically in Figure 5. Galvanic corrosion measurements were carried out for MIM steel and 316L steel couples conforming to ASTM G71-81 [64]. The test medium was artificial sweat (Table 2) described by standard EN 1811 [65] at a temperature of 37 °C, deaerated with argon. All chemicals were of reagent grade and were purchased from Merck (Darmstadt, Germany). The artificial sweat was filtered through a sterilized Falcone 0.22 mm membrane; the bottles used were of the Medical Devices type. The sweat used was not buffered with NaOH to ensure good chemical stability during corrosion testing.

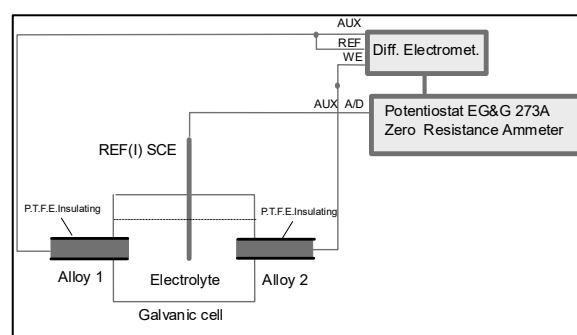


Figure 5. Electrochemical diagram of the galvanic coupling measuring cell.

Table 2. Chemical composition of artificial sweat.

Chemical Composition	Urea	NaCl	Racemic Lactic Acid
	1 ± 0.001 g/L	5 ± 0.001 g/L	940 ± 10 μ L/L

The samples were also tested in terms of pitting and crevice corrosion. The samples used for the evaluation of crevice corrosion (#3, #4 and #5) were 4 mm diameter rods (machined from the initial rods samples) driven into Teflon sample holders suitable for the crevice test technique according to ASTM F746-87 [66].

Evaluation of resistance to pitting and crevice corrosion in FeCl_3 medium. Numerous test environments for the study of pitting corrosion are described in the scientific literature. These are usually solutions of halides such as FeCl_3 , MgCl_2 , NaCl , KCl , NaF , KF , NaI , etc. The ASTM G48-11 [56] standard describes a ferric chloride (FeCl_3) test to classify stainless steels with respect to resistance at pitting and/or crevices in a medium containing chloride anions. The use of a ferric chloride solution is justified by the fact that chloride ions are known for their important role in the germination mechanism of corrosion pits and their wide distribution in the environment and in sweat. Ferric cations are also considered in the mechanism of pitting corrosion, particularly during the propagation of the pit.

The test used was adapted according to ASTM G48-11 [56]. The samples were placed in a polymerizable resin and polished to 1 mm. The test samples thus prepared were immersed in a 0.5 M FeCl_3 solution at 50 °C for 2 h. After rinsing with deionized water and ethanol p.a., the samples were examined visually and at low magnification (6×). The number of bites was counted using photographs at this magnification. The results obtained are expressed as the pit density (number of pits/cm²).

To have a comparison criterion for evaluating pitting resistance, identical samples from other steels were prepared (discs with diameters of 10 mm), as shown in Table 3. The surfaces were “mirror” polished with diamond paste with a particle size of 0.1 µm. They were tested together with the MIM steel samples.

Table 3. Standardized composition of steels tested for pitting corrosion (FeCl_3).

DIN	AISI	C	Si	Mn	P	S	Cr	Mo	Ni	Other
1.4571	316 Ti	<0.08	<1.00	<2.00	<0.045	<0.030	16.5–18.5	2.0–2.5	10.5–13.5	Ti > 5; C < 0.80
1.4435	316L	<0.030	<1.00	<2.00	<0.045	<0.025	17.0–18.5	2.5–3.0	12.5–15.0	--
SW14435	316L	<0.030	<1.00	<2.00	<0.045	<0.025	17.0–18.5	2.5–3.0	12.5–15.0	
PX14435	316L	<0.030	<1.00	<2.00	<0.045	<0.025	17.0–18.5	2.5–3.0	12.5–15.0	
1.4441	316L med.	<0.030	<1.00	<2.00	<0.025	<0.010	17.0–19.0	2.5–3.2	13.0–15.5	N < 0.10; Cu < 0.120
PM14435	316L	<0.030	<1.00	<2.00	<0.045	<0.025	17.0–18.5	2.5–3.0	12.5–15.0	
1.4539	904L	<0.02	<0.70	<2.00	<0.030	<0.015	19.0–21.0	4.0–5.0	24.0–26.0	Cu 1.00–2.00; N 0.04–0.15

Evaluation of the quantity of nickel released. The nickel release test was carried out on artificial sweat according to the EN 1811 standard [65]. The samples, polished with 0.1 mm diamond paste, were first cleaned with ethanol p.a. under ultrasound. The test tubes, containing a sample as well as 2.6 mL of artificial sweat, were kept in an oven at 30 ± 2 °C for 7 days. The nickel was then determined by ICP-AES.

3. Results and Discussion

3.1. Metallography

Figure 6 presents the surface of MIM sample #10 before and after the metallographic attack. Before the metallographic attack, the existence of porosities on the sample surface was noted. The metallographic attack also revealed small black dots, which were probably porosities in the mass of the samples, and the dendritic structure could be distinguished. According to ASTM E112-13 [67], the grain size was 4. The microstructures for all the other MIM steel samples are presented in Figure 7.

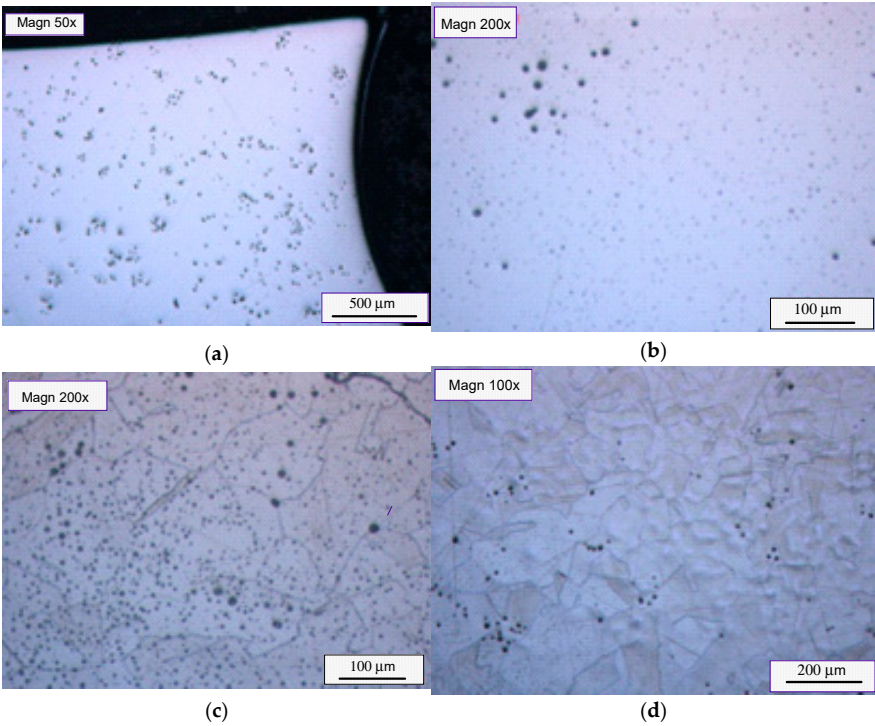


Figure 6. Surface of MIM sample #10 before (a,b) and after the metallographic attack (c,d).

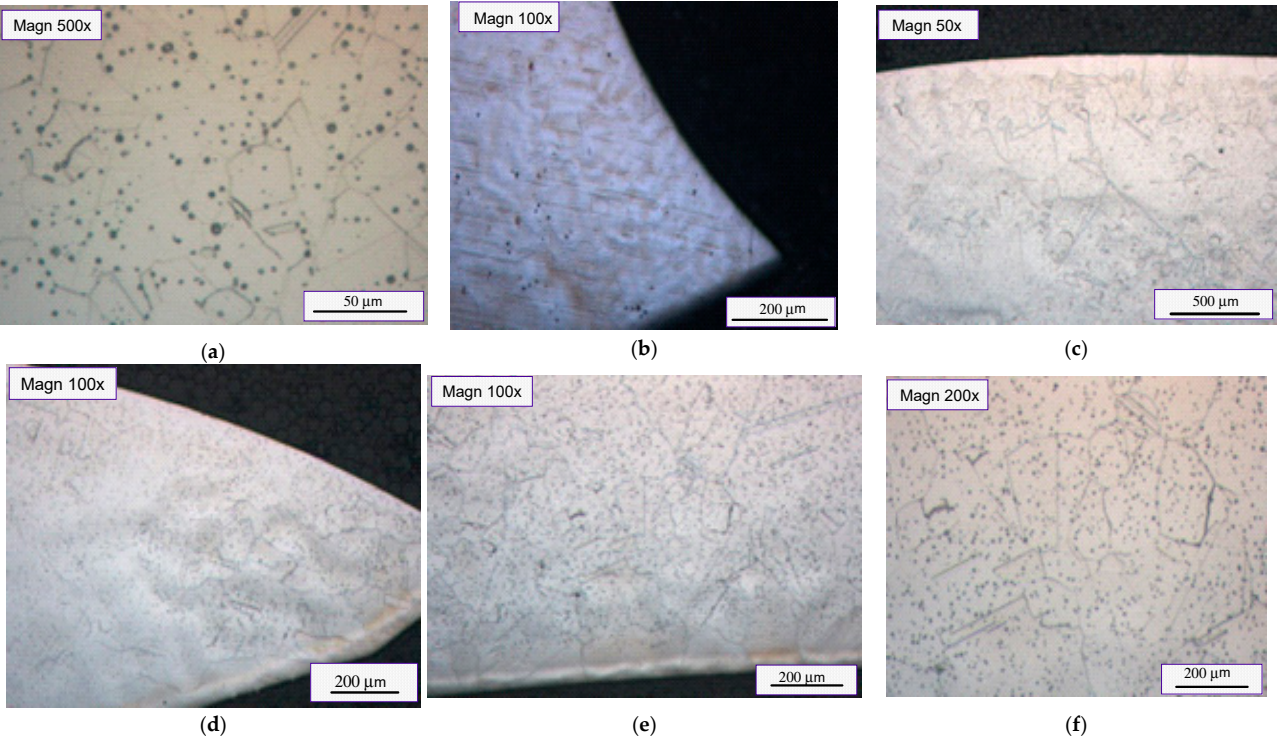


Figure 7. Cont.

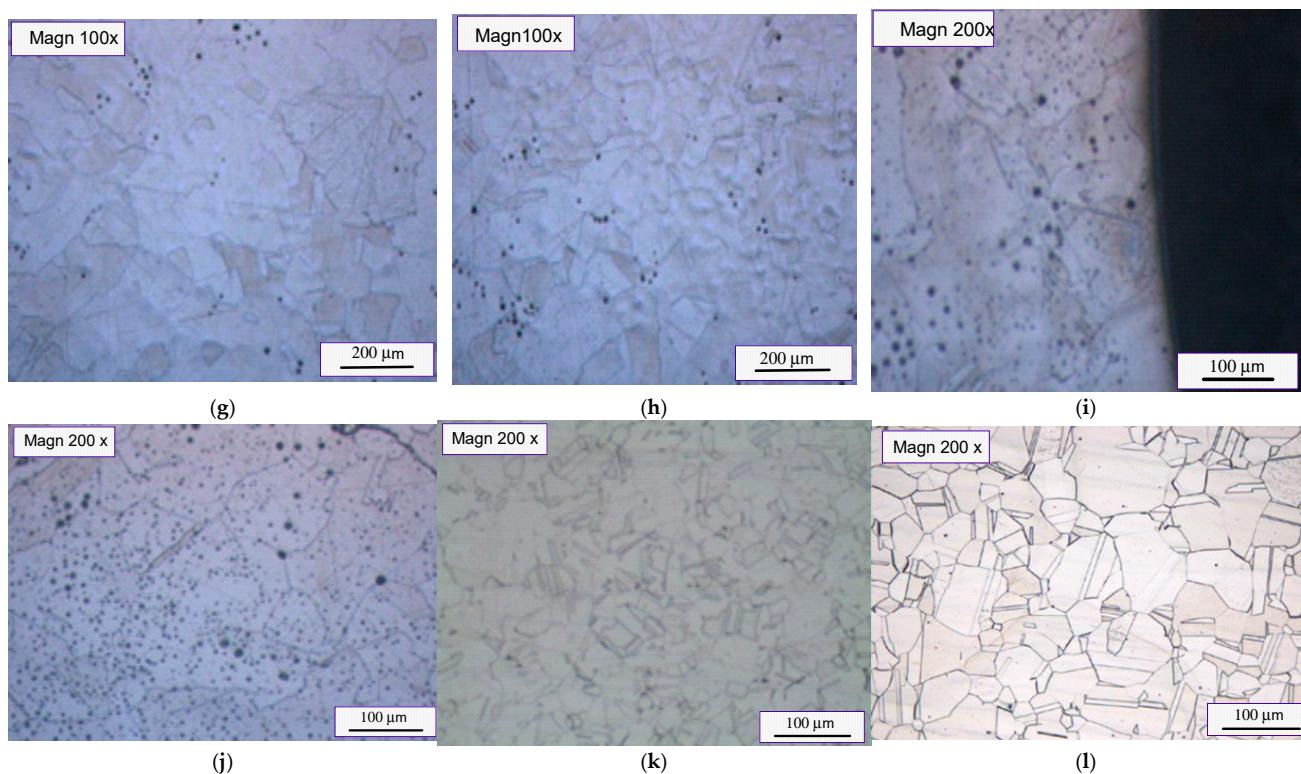


Figure 7. Surfaces of the MIM samples and standard alloys 904L and 316L after the metallographic attack: (a) #1; (b) #2; (c) #3; (d) #4; (e) #5; (f) #6; (g) #7; (h) #8; (i) #9; (j) #10; (k) AISI 904L: grain size 7; (l) AISI 316L: grain size 5.

There are phenomenological changes that occur during sintering, which were noted in all the structures shown in Figure 7. The structure is completely homogeneous, it is a visible embedded dendritic structure with spheroidal porosity and considerable grain growth. The original particle boundaries completely disappear with the formation of a single-phase austenitic structure, peppered with annealing twins [68]. For the comparison criteria, Figure 7 also presents the structures of the AISI 316L and AISI 904L steels.

3.2. Corrosion Behavior Evaluation Using Electrochemical Techniques

Generalized corrosion. The open circuit potential curves as a function of time for MIM steels are presented in Figure 8. After 16 h of immersion, the MIM steels showed a tendency toward passivation, and their E_{oc} potential stabilized in the cathodic domain (positive values). Only for sample #2, the E_{oc} remained in the anodic domain. For samples #9 and #10, disturbances were noted, most likely caused by surface phenomena such as passivation–depassivation in a non-stationary immersion regime.

The calculated values of R_p , i_{corr} and Tafel slopes are presented in Table 4. For a comparative image, the electrochemical parameters of the 316L and 904L steels are introduced in the same table. For all the results, it was noticed that MIM steels presented an inferior corrosion behavior compared to 316L and 904L steels. It is very difficult to envisage a certain trend in relation to the technological parameters taken into consideration in Figure 2. The dispersion of results is too important.

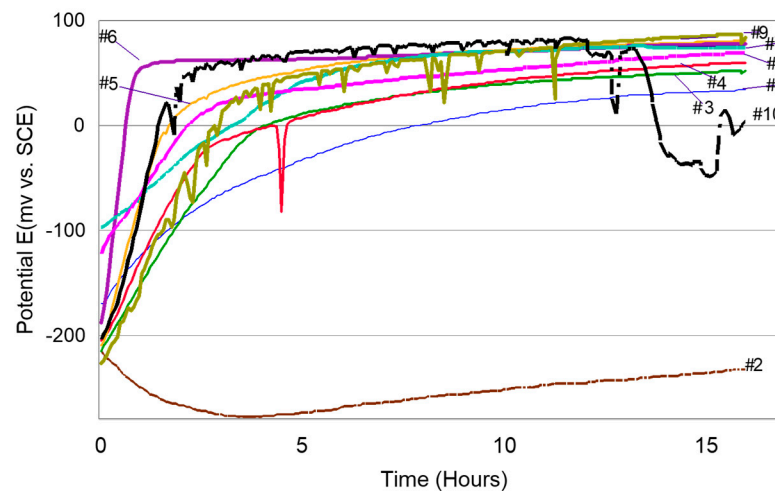


Figure 8. Open circuit potential (E_{oc}) curves as a function of time for the tested MIM steels.

Table 4. Electrochemical parameters measured and calculated for MIM steels and for 316L and 904L standard steels.

Samples Tested		$E (i = 0)$	R_p	b_c	b_a	i_{corr}	Coulometric Analysis	
							$E_{corr} - 300 \text{ mV}$	$300 \text{ mV} - 600 \text{ mV}$
		mV	kOhm.cm ²	mV/Decade	mV/Decade	nA/cm ²	mC/cm ²	mC/cm ²
316L		32	1507	414	113	27	1.96	198.0
904L		123	347	122	312	91	2.52	20.65
#1	S+HIP	33	552	244	102	31	1.15	1691.0
#2	S+HIP	−233	232	46	76	226	4.40	1300.0
#4	S+HIP	67	290	545	52	85	1.07	1304.0
#6	S+HIP	83	115	69	113	568	7.51	2354.0
#7	S+HIP	60	80	589	39	654	4.02	4.10
#8	S+HIP	72	55	252	52	777	2.16	3.70
#3	S	66	290	97	77	151	1.02	864.4
#5	S	76	53	92	47	528	1.82	1212.0
#9	S	74	45	251	39	931	1.23	663.5
#10	S	36	96	69	181	340	2.11	1503.0

Linear-version potentiodynamic polarization curves plotted between -1000 mV and $+1000 \text{ mV}$ ECS for MIM steels are presented in Figure 9. It can be noted that the curves reveal better corrosion behavior for the 904L MIM steels (#7 and #8) compared to all the 316L MIM steels.

The breakdown potentials of MIM type 316L steels were between 250 and 400 mV (Figure 9b). For samples #5, #6, #9 and #10, degradation peaks (spikes) were observed at 100 mV. For samples #1, #2 and #3, anodic current values at -100 mV were revealed. The shape of the curves indicated the presence of numerous disturbances that were specific to pitting and crevicing phenomena.

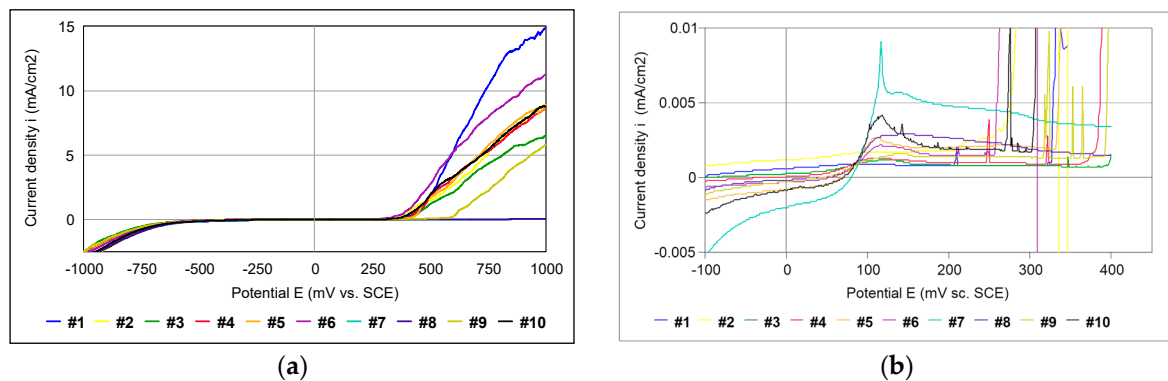


Figure 9. (a) Potentiodynamic polarization curves obtained for MIM steels—linear version; (b) Zoom in the area of the breakdown potentials.

The potentiodynamic curves of an MIM steel and a classic 316L steel are presented in Figure 10. Its potentiodynamic curve was traced under the same experimental conditions. It should be noted that the 316L steel showed better generalized corrosion behavior.

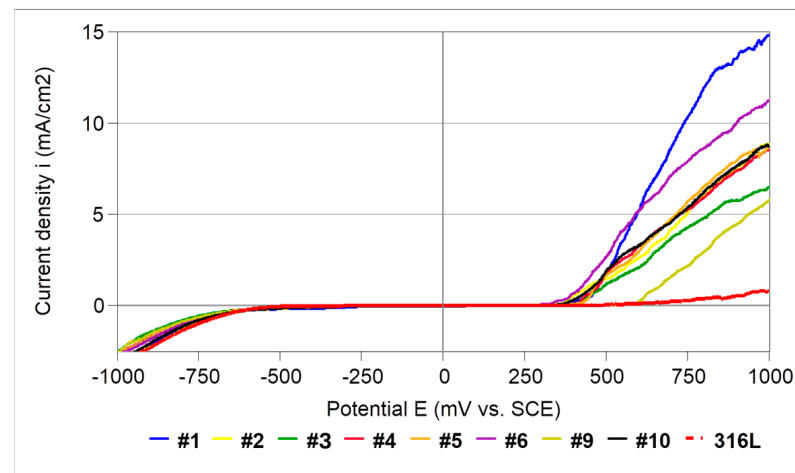


Figure 10. Comparison of the potentiodynamic polarisation curves of MIM 316L steels with 316L steel measured under the same experimental conditions.

In the same way, potentiodynamic curves were drawn for the 904L alloys: MIM samples #1 and #8 versus the classic 904L sample, as shown in Figure 11a. From the same experimental conditions, the 904L classic steel presented better corrosion behavior, as shown in Figure 11b. In the same area, the MIM steels showed peaks at 100 mV; this is the beginning of pitting or crevice corrosion phenomena. However, in the region of 400 mV to 800 mV, the best behavior was revealed by MIM steels. Due to a lack of samples, the laboratory did not conduct specific pitting and crevice corrosion tests other than those according to ASTM F746-87 [66]. The 904L steel in the anodic region revealed an increase in current from a potential of 400 mV. This displacement was specific to the process of pitting and crevice corrosion morphology. Current disturbances noted between 400 and 800 mV were due to the pin hole propagation process. The breakdown potentials were around 800 mV ECS.

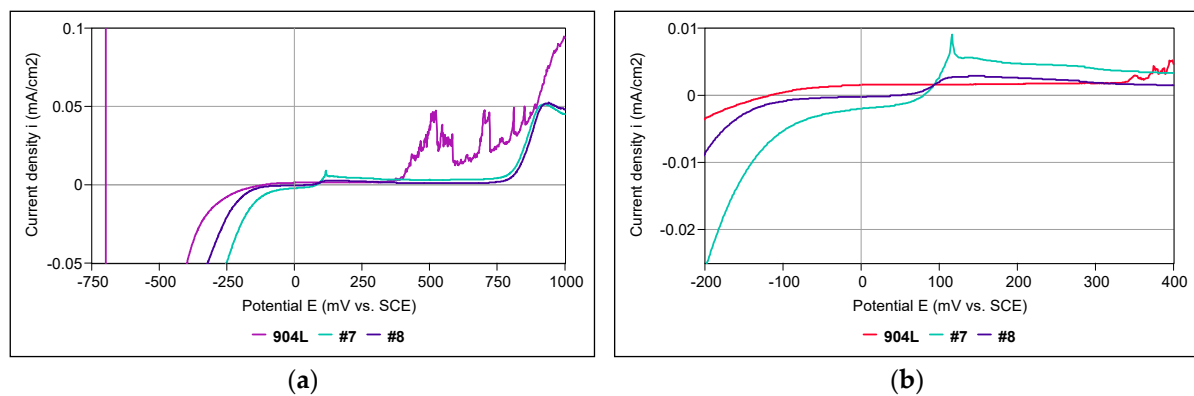


Figure 11. (a) Comparison of the potentiodynamic polarization curves of MIM 904L steels with 904L steel measured under the same experimental conditions. (b) Zoom in the area of -200 mV to $+400$ mV.

The coulometric analysis of the steels studied for the zones E_{corr} to 300 mV and 300 mV at 600 mV is presented in Table 5. It also confirms the observations and remarks made according to the electrochemical parameters presented previously. In the family of MIM samples, the best behavior was noted for the 904L steels (#7 and #8). From this criterion, the comparison of MIM 316L steels does not allow correlations to be drawn with the technological manufacturing parameters presented in Figure 4.

Table 5. Quantity of electrical charge delivered for 72 h of galvanic coupling.

Galvanic Couple MIM Steel/316L AISI	Quantity of Electrical Charge Delivered for 72 h [C/cm ²]
MIM #1/316L AISI	3.69
MIM #3/316L AISI	0.25
MIM #4/316L AISI	1.24
MIM #5/316L AISI	0.22
MIM #6/316L AISI	2.12
MIM #7/904L AISI	3.23
MIM #8/904L AISI	0.17
MIM #9/316L AISI	2.97

The rotating electrode technique was used to highlight the morphologies of pitting and crevice corrosion. The rotation speed applied was 300 rpm to ensure the presence in a laminar hydrodynamic regime (laminar flow) with a Reynolds criterion value (Re) of 3200 . The test was carried out with a low scanning speed of 0.03 mV/s. The polarization curves were plotted in pseudo-stationary regime, as shown in Figure 12. The anodic current increased sharply at the pitting potential, which is also called breakdown potential, E_{bd} [69].

Between the increasing domain of the current, 10^{-6} A and 10^{-4} A, there were noted two stages. The first stage corresponded to pit initiation, and the second one from the E_{bd} corresponded to pit propagation. The two tested MIM grades, 316L and 904L, presented different levels of propagation in relation to the electric potential: for MIM 316L alloys, $E = 106$ mV et $I = 16 \times 10^{-6}$ A/cm², and for MIM 904L alloys, $E = 367$ mV and $I = 1.74 \times 10^{-6}$ A/cm², as shown in Figure 13.

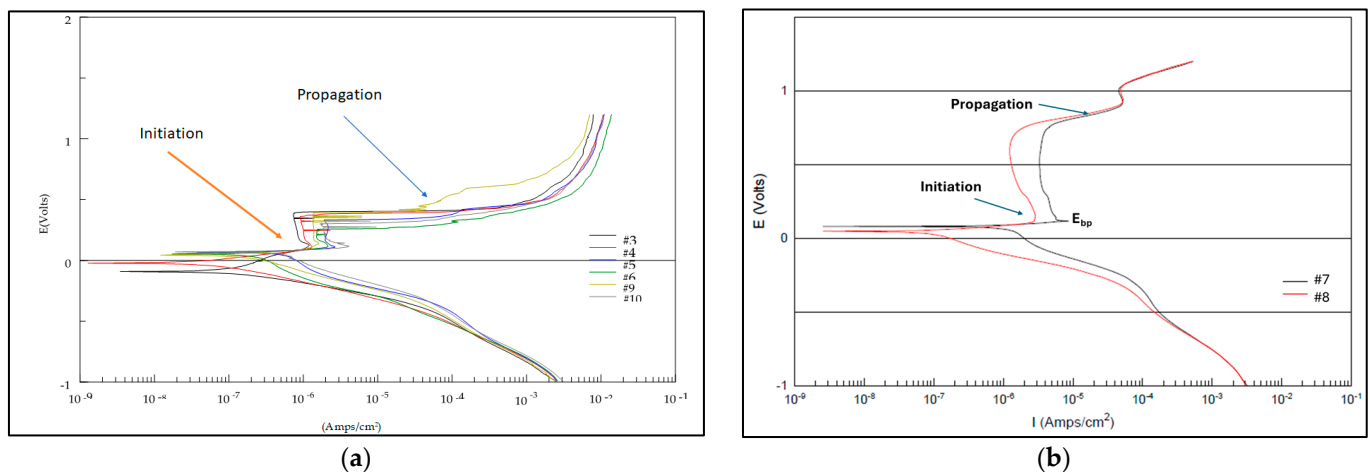


Figure 12. Potentiodynamic polarization curves obtained for the MIM steels, semi-logarithm axis: (a) MIM 316L samples (b) MIM 904L samples.

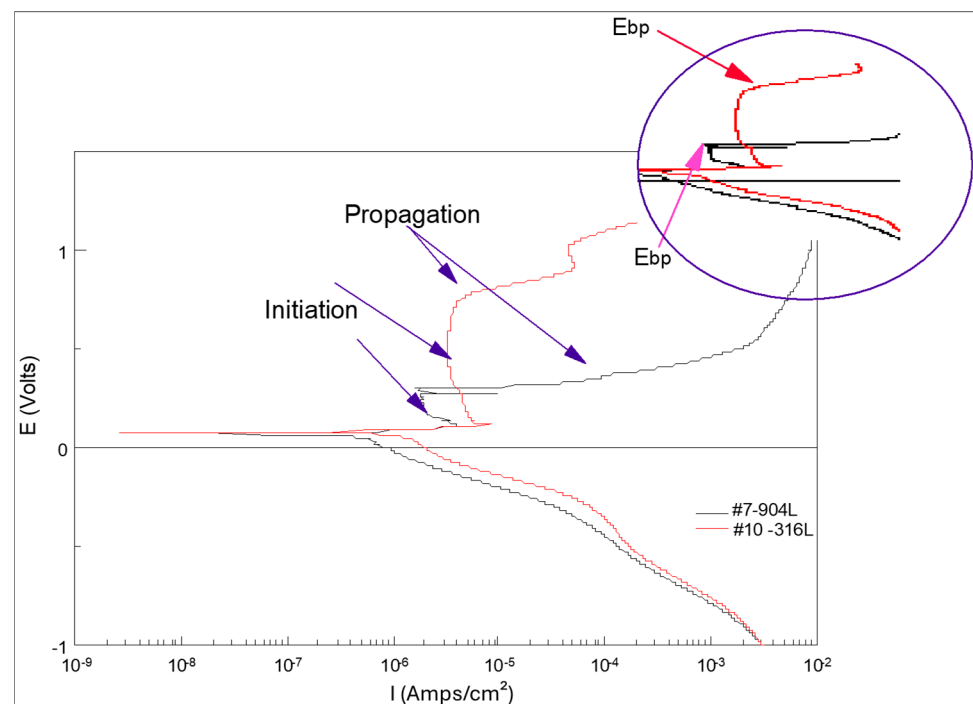


Figure 13. Pit initiation and propagation stages for #10 and 316L and #7 and 904L alloys.

According to bibliographic data mentioned in this study, the value of the pitting potential (E_{bd}) does not correspond to a well-defined thermodynamic or kinetic parameter. It depends both on the initiation processes and on the kinetics of propagation and re-passivation. Being a property of the metal–environment system, the E_{bd} depends in particular on: the chemical nature and microstructure of the metal, the surface condition, the presence of inclusions, the chemical composition and nature of the electrolyte, temperature and convection conditions.

The morphologies of pitting and crevice corrosion were highlighted by microscope investigations after the potentiodynamic polarization tests. Figure 14 presents the images of all the tested alloys. It can be noted that all the steels revealed a high sensitivity to this form of morphology.

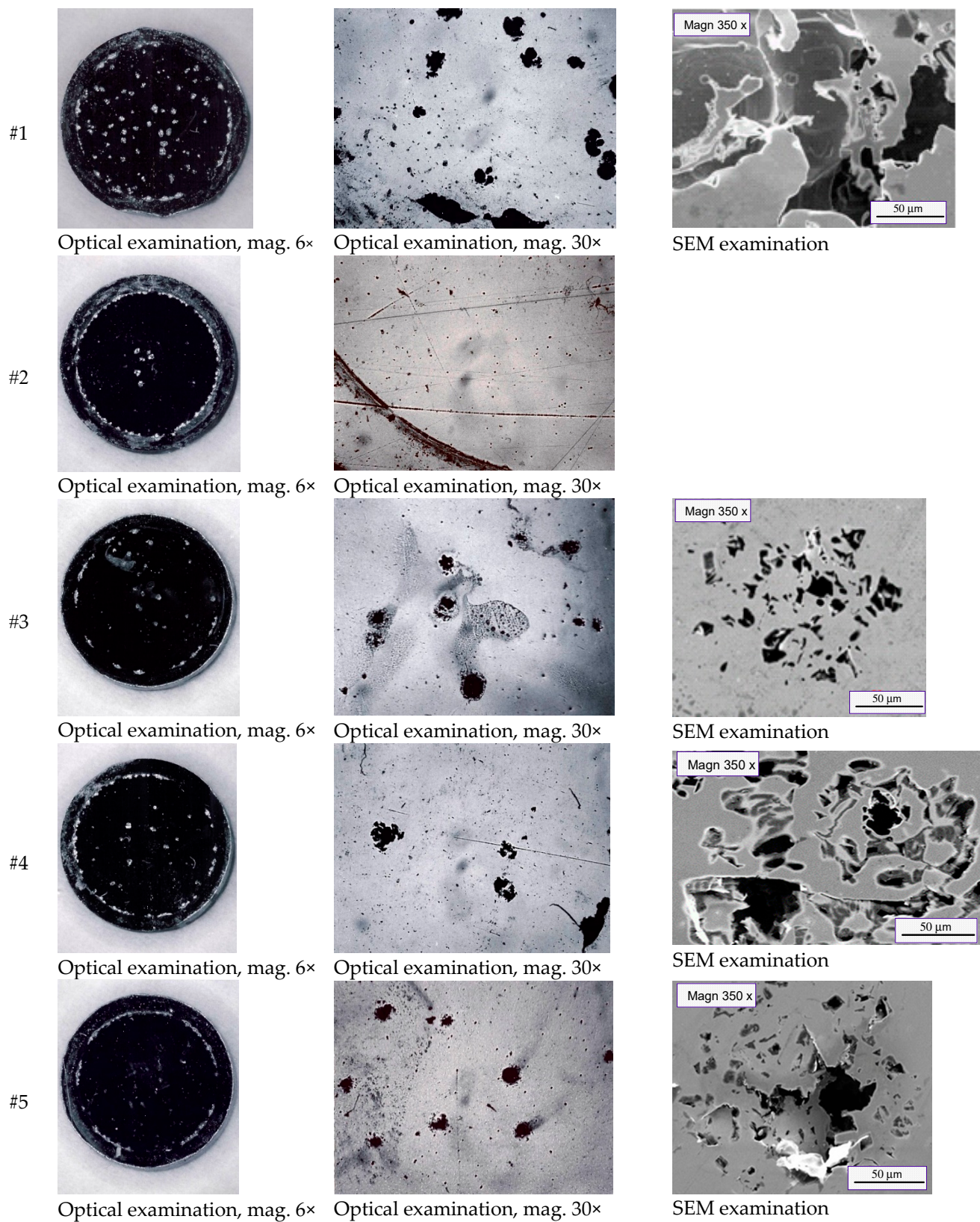


Figure 14. Cont.

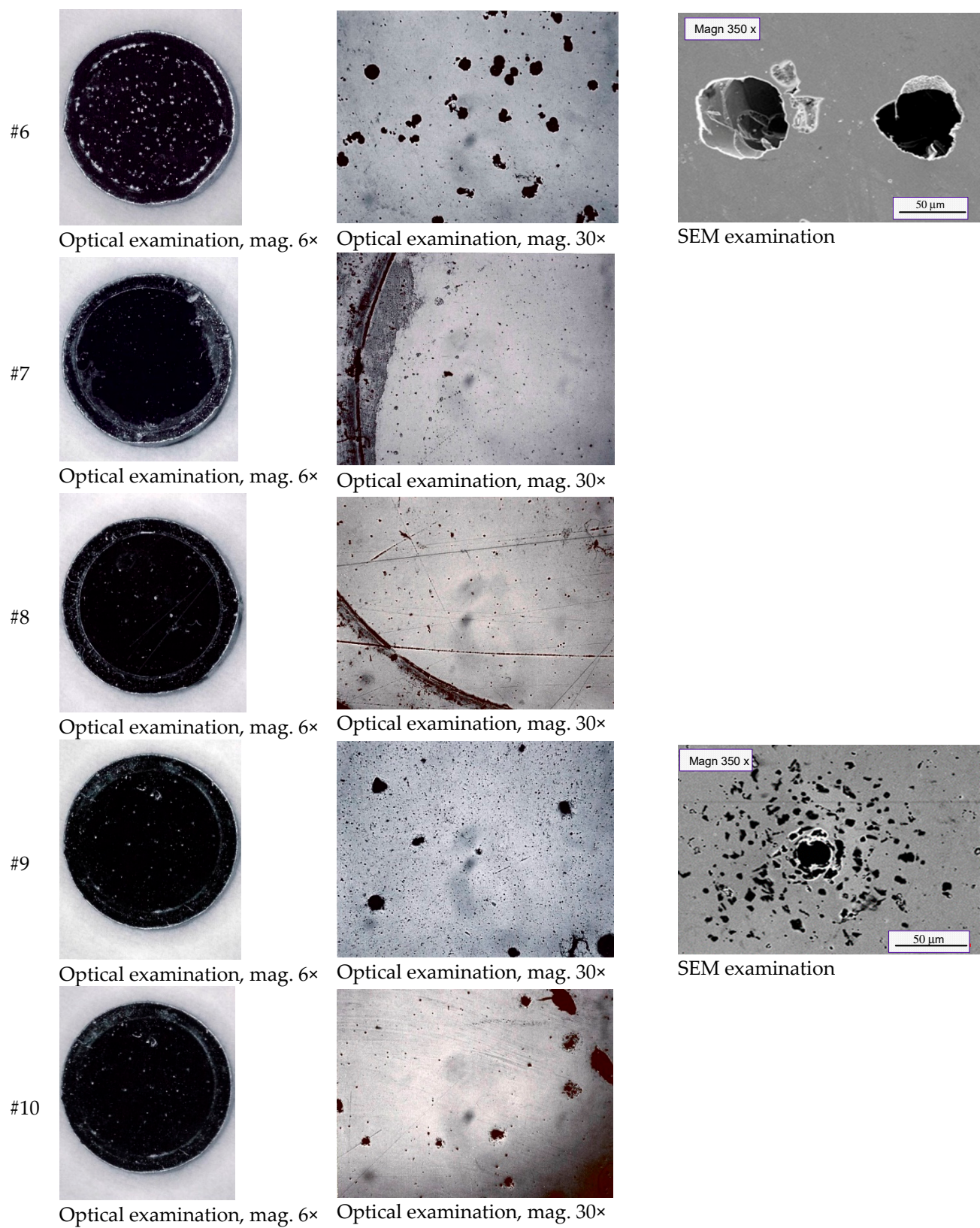


Figure 14. Optical and electron microphotographs of MIM samples after potentiodynamic polarization tests.

Figure 15 presents a zoom of a pit that highlights the metallic particles of the feedstock (red arrows). In this case, it can be considered an MIM composite mass and not a homogeneous metallic mass in which all metallic particles should be dissolved.

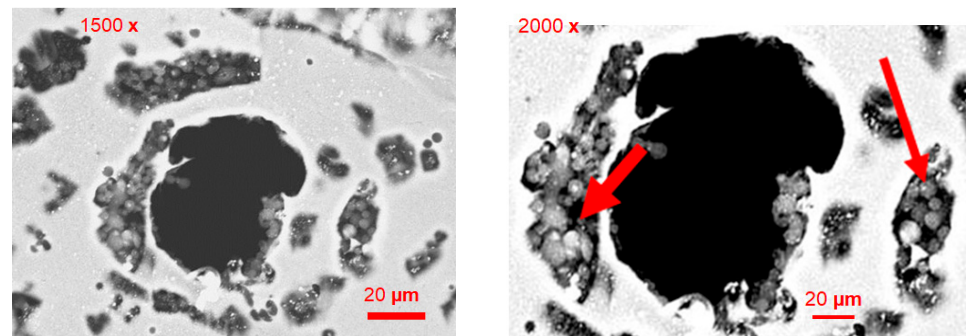


Figure 15. MIM 316L steel, #9—Feedstock particles presented in corrosion pits. SEM magnification 1500× and zoom 2000×.

Galvanic corrosion evaluation. The galvanic coupling currents measured for the MIM 316L samples (#1, #3, #4, #5, #6 and #9) with 316L AISI steel as a coupling partner and MIM 904L (#7, #8) coupling with 316L AISI are presented in Figure 16. A strong dispersion of the results can be observed, with current values up to 15 $\mu\text{A}/\text{cm}^2$. The disturbances noted on the curves reveal the presence of localized corrosion processes (pitting and crevices). Examination of the surfaces of the tested samples showed important degradation of the MIM steel surfaces compared with those of the 316L AISI steel.

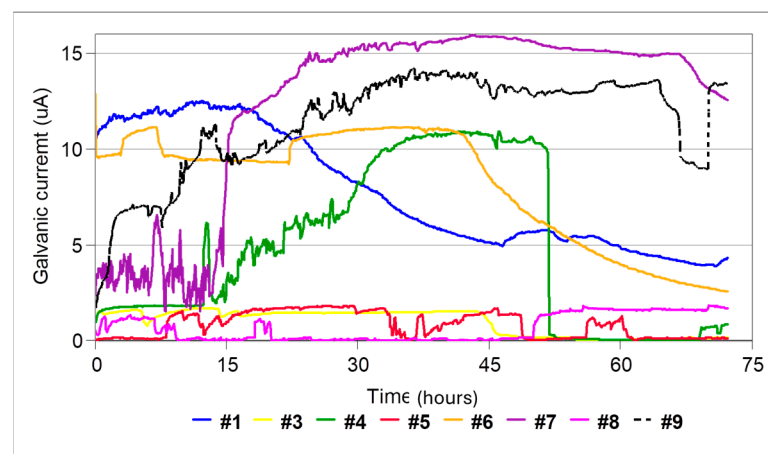


Figure 16. Galvanic coupling currents measured for 72 h between MIM 316L (#1, #3, #4, #5, #6, #9) and 316L AISI steel and 904L MIM (#7, #8) and 316L AISI steel.

In general, to reduce the galvanic cell effect, galvanic couplings must deliver quantities of electrical charge of micro and even nanocoulomb orders. Table 5 presents the calculated quantity of electrical charge delivered in the couplings for 72 h. These quantities were high, in the order of coulombs for MIM steels 316L #1, #4, #7 and #9 and in the order of hundreds of millicoulombs for MIM steels 316L #3, #6 and #8. Finally, the corrosion process triggered by the couplings generated surface damage with releases of cations. There was certainly a reason why samples #3, #5 and #8 discharged less electrical charge, but it was not related to the parameters shown in the diagram in Figure 2.

In summary, the technological parameters chosen to characterize MIM steels do not highlight the possibility of a discriminant analysis regarding their corrosion behavior. It is noted that the MIM type 904L steels presented better behavior compared to MIM 316L steels. Conventional steels studied under the same experimental conditions revealed better behavior compared to MIM steels independently of the phenomenological parameters chosen.

Pitting corrosion evaluation using the FeCl_3 medium. Figure 17 presents the pitting corrosion assessment test results for MIM samples in parallel with those obtained for a series of conventional steels (Table 3). It is noted that the MIM stainless steels were affected more than the conventional steels.

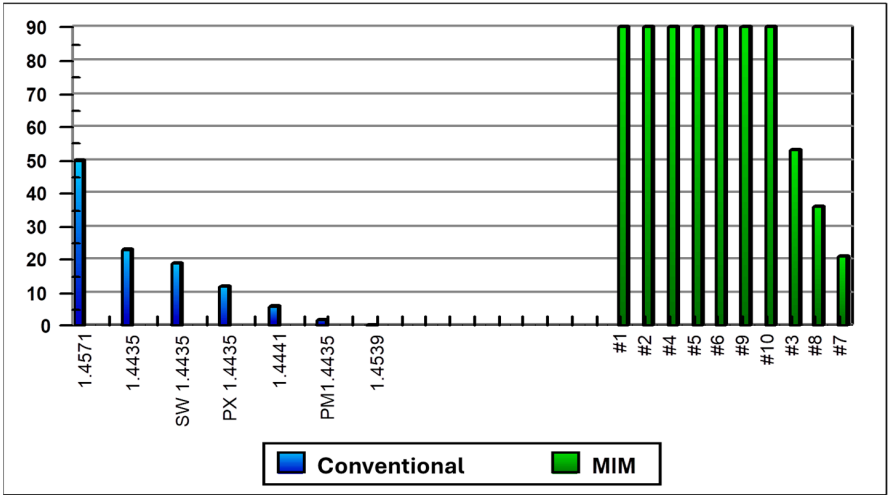


Figure 17. Evaluation of the pit density (number.cm⁻²) after the ferric chloride test (FeCl_3 , 2 h at 50 °C).

MIM samples #5, #9 and #10 presented corrosion pits on their surface that were easily visible to the naked eye. According to Figure 18, the following trends can be identified: MIM samples #1, #2, #4, #5, #6, #9 and #10 presented the worst pitting corrosion behavior in terms of pitting density, and samples #7 and #8 (904L) presented the best. MIM steel #3 represented an intermediate case.

According to the results obtained, MIM 904L steels are comparable with conventional 316L steels in terms of their resistance to pitting corrosion, as shown in Figure 17. All samples suffered from crevice corrosion at the alloy–resin interface, as shown in Figure 18.

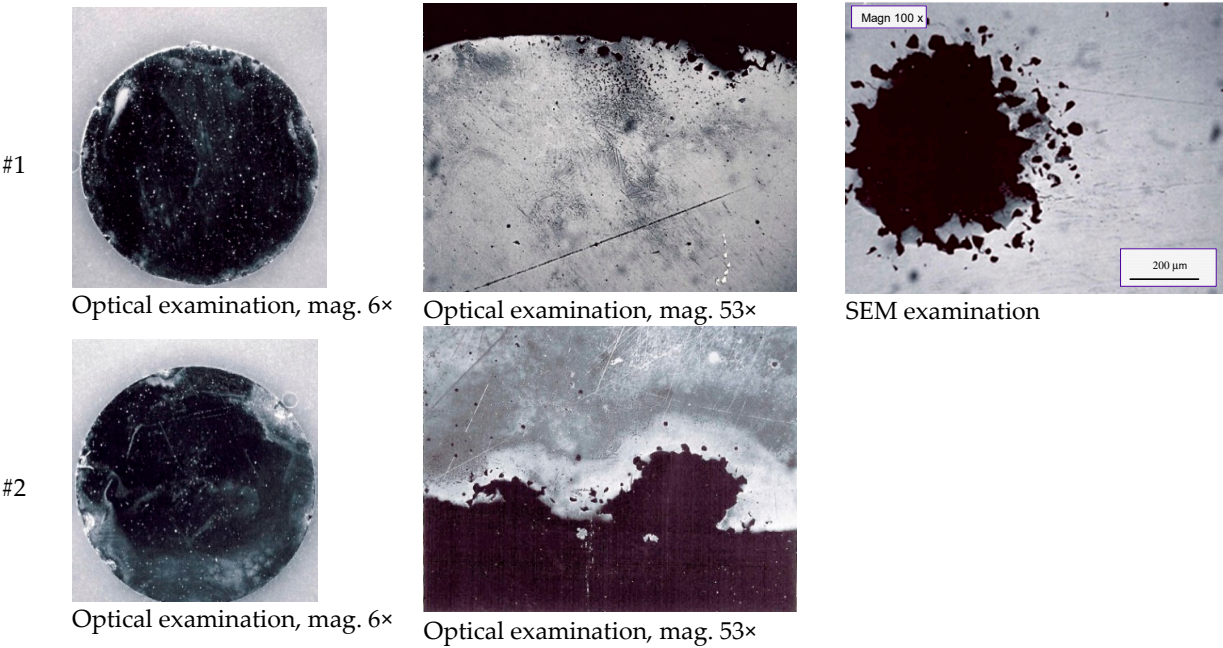


Figure 18. Cont.

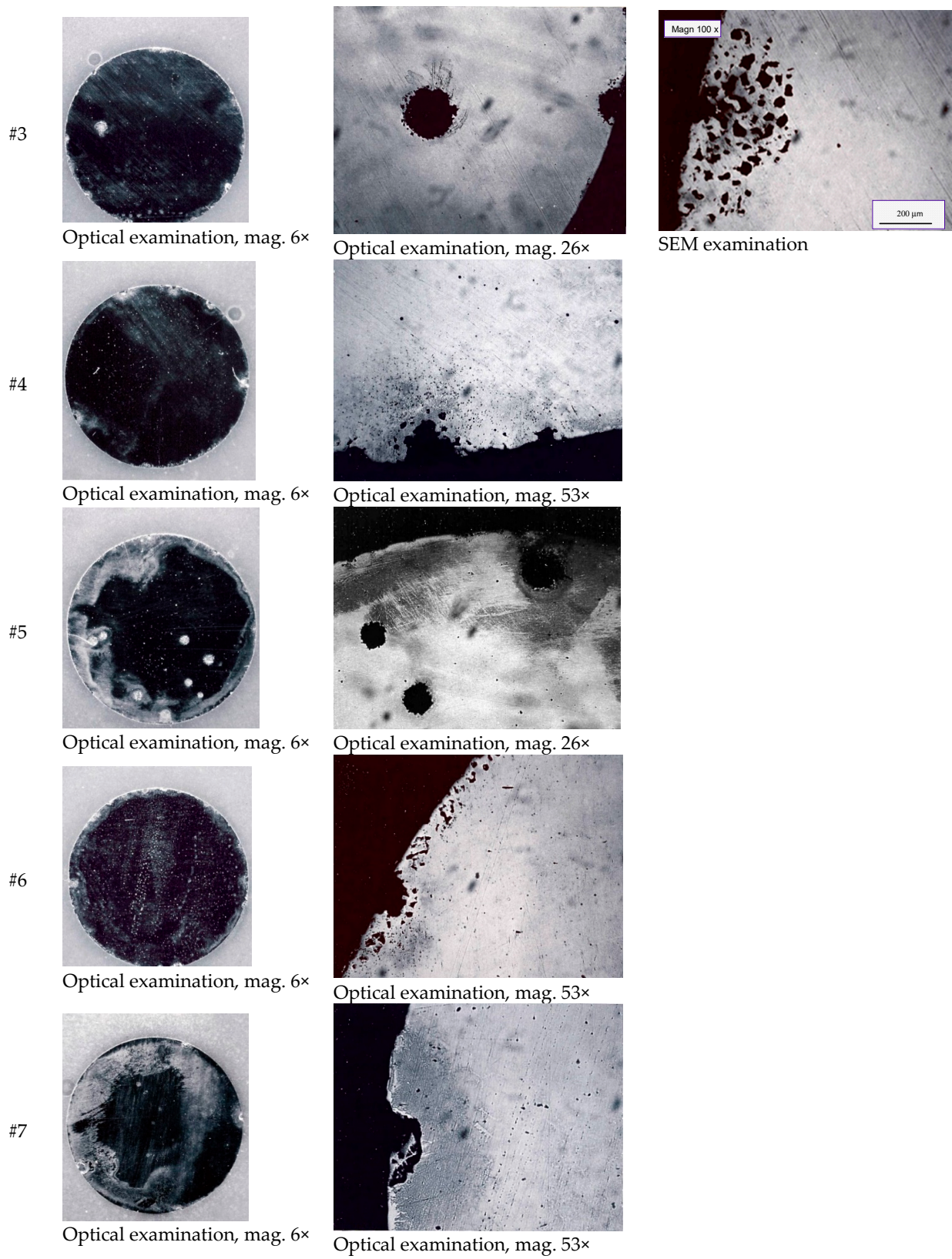


Figure 18. Cont.

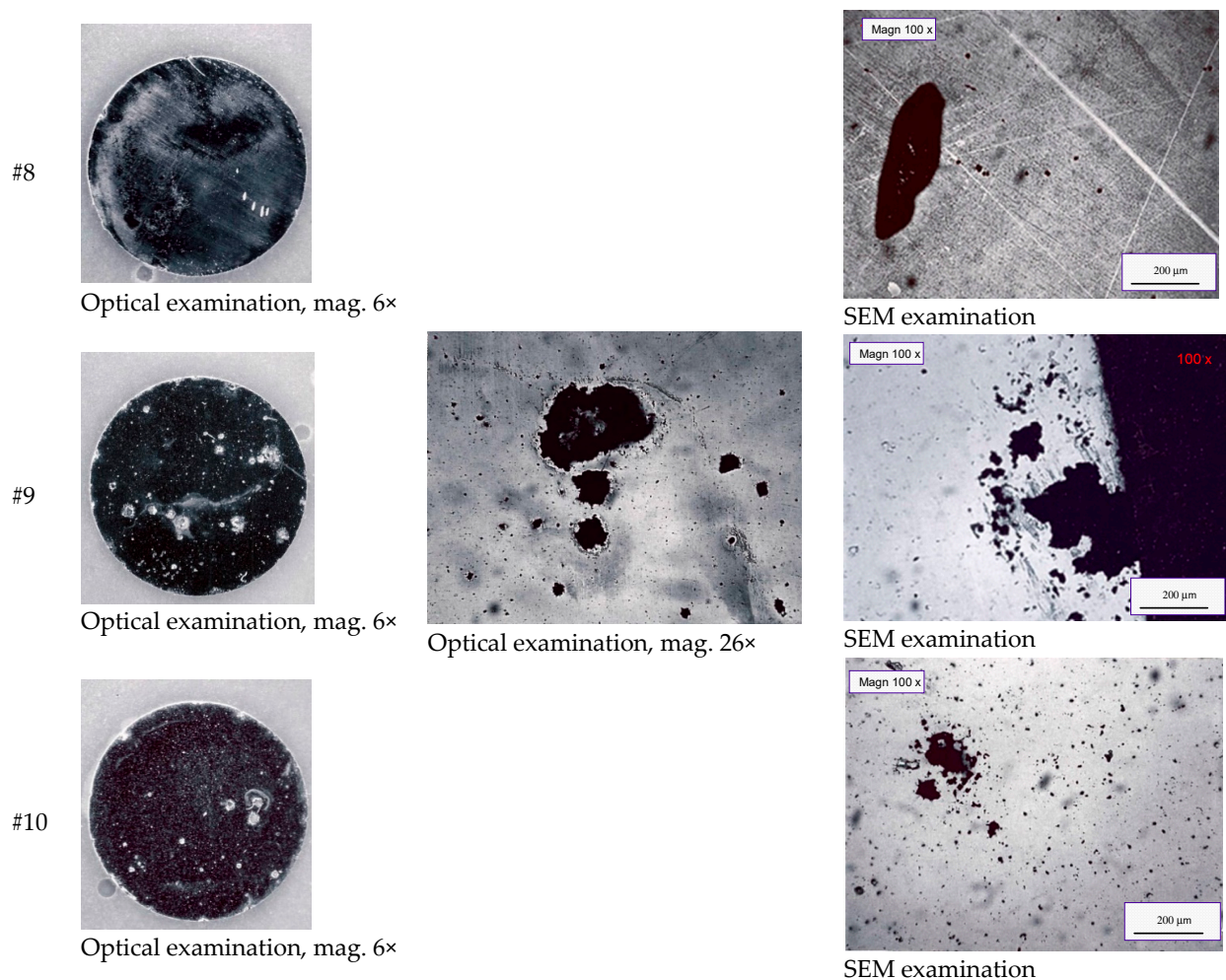


Figure 18. Optical and electron microphotographs of MIM samples after FeCl_3 media test (0.5 M, 2 h at 50 °C).

Release of nickel cations. The released nickel cations calculated for the MIM alloys and for two conventional 316L and 904L alloys are presented in Figure 19. In the case of the MIM alloys, the quantities of nickel released were very significant; they varied from $2 \text{ mg.cm}^{-2}.\text{week}^{-1}$ up to $24 \text{ mg.cm}^{-2}.\text{week}^{-1}$. For the two conventional alloys, the released nickel cations were very low. Those for 904L steel was measured at $0.25 \text{ mg.cm}^{-2}.\text{week}^{-1}$, and those for 316L steel was measured at $0.35 \text{ mg.cm}^{-2}.\text{week}^{-1}$, similar to the medical applications alloys.

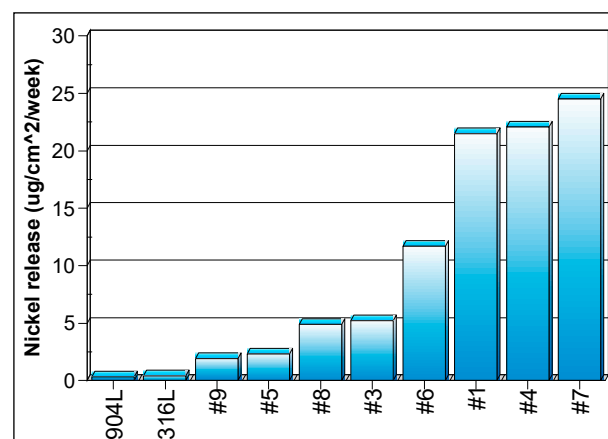


Figure 19. Nickel cations released according to EN1811 [65].

4. Conclusions

The evaluation of corrosion resistance of ten MIM alloys (eight samples of MIM type 316L and two samples of MIM type 904L) was studied using electrochemical techniques, rotating electrodes and galvanic coupling. Different electrochemical parameters were measured and calculated (the open circuit potential, the polarization resistance, the corrosion current and Tafel slopes, the coulometric analysis and galvanic coupling current). A test to evaluate their resistance to pitting corrosion in a ferric chloride medium and the measure of the released nickel cations were completed in this study.

The following conclusions can be drawn from all the results:

- The measured and calculated electrochemical quantities showed the presence of localized pitting and crevice corrosion processes between 100 and 400 mV. Unfortunately, due to a lack of samples specific to the localized corrosion test, our laboratory was unable to precisely determine and analyze this type of behavior. Generally, if MIM steels are compared with conventional steels, their corrosion resistance behaviors were noted to be inferior.
- In the couplings studied, the galvanic currents generated were very important. The shape of the curves also revealed the presence of localized corrosion phenomena.
- According to tests in ferric chloride, for the MIM steels, inferior behavior was noted compared to conventional steels. MIM type 904L steels were comparable in behavior to conventional type 316L steels.
- The quantities of nickel released according to EN 1811 were very significant and did not meet the requirements of the European directive of $0.5 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{week}^{-1}$.
- The parameters studied to characterize corrosion behavior did not reveal any correlation with the manufacturing parameters proposed as technological criteria.

Today, there is a strong trend of developing nickel-free steels that need adhere to the ASTM standard F2229-02 designating a “Standard Specification for Wrought, Nitrogen Strengthened 23Mn-21Cr-1Mo Low-Nickel Stainless Steel Alloy Bar and Wire for Surgical Implants” [70]. A certain number of other nominally nickel-free austenitic steels are also stabilized with nitrogen and manganese. This is an open door for the development of MIM steels that can be used for articles in contact with the human body.

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References

1. Suwanpreecha, C.; Manonukul, A.A. Review on Material Extrusion Additive Manufacturing of Metal and How It Compares with Metal Injection Moulding. *Metals* **2022**, *12*, 429. [[CrossRef](#)]
2. Hwang, I.-S.; So, T.-Y.; Lee, D.-H.; Shin, C.-S. Characterization of Mechanical Properties and Grain Size of Stainless Steel 316L via Metal Powder Injection Molding. *Materials* **2023**, *16*, 2144. [[CrossRef](#)] [[PubMed](#)]
3. Widianegara, I.P.; Putri, R.A.K.; Han, D.I.; Bahanan, W.; Lee, E.H.; Woo, C.H.; Kang, J.-H.; Ryu, J.; Ko, Y.G. Characterization of Green Part of Steel from Metal Injection Molding: An Analysis Using Moldflow. *Materials* **2023**, *16*, 2516. [[CrossRef](#)]
4. Yi, J.H.; Shi, W.F. The technology of metal powder injection molding and its development. *Min. Metall. Eng.* **2001**, *21*, 4–8.
5. Su, S.; Hong, Z.; Huang, Y.; Wang, P.; Li, X.; Wu, J.; Wu, Y. Integrated Numerical Simulations and Experimental Measurements for the Sintering Process of Injection-Molded Ti-6Al-4V Alloy. *Materials* **2022**, *15*, 8109. [[CrossRef](#)] [[PubMed](#)]
6. Langlais, D.; Demers, V.; Brailovski, V. Rheology of dry powders and metal injection molding feedstocks formulated on their base. *Powder Technol.* **2022**, *396*, 13–26. [[CrossRef](#)]

7. Hu, C.; Hg, H.; Fan, B.; Li, J.; Wang, T.; Li, D.; Li, Y. Biocompatibility of vascular stents manufactured using metal injection molding in animal experiments. *Trans. Nonferrous Met. Soc. China* **2022**, *32*, 569–580.
8. Hamidi, M.F.F.A.; Harun, W.S.W.; Samykano, M.; Ghani, S.A.C.; Ghazalli, Z.; Ahmad, F.; Sulong, A.B. A review of biocompatible metal injection moulding process parameters for biomedical applications. *Mater. Sci. Eng. C* **2017**, *78*, 1263–1276. [[CrossRef](#)]
9. Dehghan-Manshadi, A.; Yu, P.; Dargusch, M.; StJohn, D.; Qian, M. Metal injection moulding of surgical tools, biomaterials and medical devices: A review. *Powder Technol.* **2020**, *15*, 189–204. [[CrossRef](#)]
10. Gross, M.; Motivans, L. Medical Device Materials Bimetallic MIM medical components. *Mater. Process. Med. Devices* **2003**, 403–407.
11. Zhang, W.; Li, L.; Huang, C.; Ngai, T.; Hu, L. Effect of Sintering Temperature and Solution Treatment on Phase Changes and Mechanical Properties of High-Nitrogen Stainless Steel Prepared by MIM. *Materials* **2023**, *16*, 2135. [[CrossRef](#)] [[PubMed](#)]
12. Prathab Rao, M.; Ibrahim, M.H.I.; Amin, S.Y.M.; Othman, M.H. Parameter optimization of metal injection moulding: A review. *J. Mech. Eng.* **2018**, *5*, 100–114.
13. Basir, A.; Muhamad, N.; Sulong, A.B.; Jamadon, N.H.; Foudzi, F.M. Recent Advances in Processing of Titanium and Titanium Alloys through Metal Injection Molding for Biomedical Applications: 2013–2022. *Materials* **2023**, *16*, 3991. [[CrossRef](#)] [[PubMed](#)]
14. Dehghan-Manshadi, A.; Chen, Y.; Shi, Z.; Bermingham, M.; StJohn, D.; Dargusch, M.; Qian, M. Porous titanium scaffolds fabricated by metal injection moulding for biomedical applications. *Materials* **2018**, *11*, 1573. [[CrossRef](#)] [[PubMed](#)]
15. D’Andrea, D. Additive Manufacturing of AISI 316L Stainless Steel: A Review. *Metals* **2023**, *13*, 1370. [[CrossRef](#)]
16. Santonocito, D.; Fintova, S.; Di Cocco, V.; Iacoviello, F.; Risitano, G.; D’Andrea, D. Comparison on mechanical behavior and microstructural features between traditional and AM SISI 316L. *Fatigue Fract. Eng. Mater. Struct.* **2022**, *46*, 379–395. [[CrossRef](#)]
17. Liu, C.; Kong, X.; Kuang, C.; Fenmo, Y.J. Research on powder injection molding of grade 2 CP-titanium for biomedical application. *Powder Metall. Technol.* **2016**, *34*, 281–284+290.
18. Horke, K.; Singer, R. High Cycle Fatigue of Titanium fabricated by Metal Injection Moulding (MIM). In Proceedings of the International Powder Metallurgy Congress and Exhibition, Euro PM 2013, Gothenburg, Sweden, 15–18 September 2013.
19. Kearns, M.; Johnston, M.; Murray, K.; Davies, P.; Ryabinin, V.; Gonzalez, E. Studies on the effects of niobium on sintering and properties of MIM 440C made by prealloy and master-Alloy routes E. *Int. J. Powder Metall.* **2016**, *52*, 15–24.
20. Ytoh, Y.; Miura, H. Fabrication of high strength Ti alloy compacts by metal injection molding. *J. Jpn. Soc. Powder Powder Metall.* **2016**, *63*, 438–444. [[CrossRef](#)]
21. Johari, N.; Sauti, R.; Abdullah, N.; Mohd Zainon, N.; Meh, B.; Abd Jalil, M.; Mohd Hijazi, M.; Omar, A.; Omar, M.; Baharuddin, M.Y.; et al. Physical and Mechanical Properties of Injection Molded Co-Cr-Mo Alloy Powder for Orthopedic Applications. *Adv. Mater. Res.* **2016**, *1133*, 80–84. [[CrossRef](#)]
22. Sagara, K.; Nishida, M.; Kang, H.; Tsumori, F.; Miura, H.; Nakayama, H. Fabrication of super-elastic Ti-10V-2Fe-3Al alloy compacts by MIM process. *J. Jpn. Soc. Powder Powder Metall.* **2011**, *58*, 361–366. [[CrossRef](#)]
23. Kearns, M.; Murray, K.; Davies, P.; Johnston, M.; Ryabinin, V.; Gonzalez, E. Processing and properties of MIM 430L(Nb) made by Prealloy and Master Alloy Routes Advances. In Proceedings of the European Congress and Exhibition on Powder Metallurgy, Milan, Italy, 1–5 September 2017; pp. 331–340.
24. Muterlle, P.; Perina, M.; Molinari, A. MIM of Co alloy for biomedical applications. In *Injection Molding: Process, Design, and Applications*; Nova Science Publishers: Hauppauge, NY, USA, 2011; pp. 185–218.
25. Lin, B.; Duan, B.; Qu, X. Effects of different powders on the properties of heat-resistant alloys prepared by metal injection molding. *J. Univ. Sci. Technol.* **2008**, *30*, 1024–1028.
26. Virdhian, S.; Osada, T.; Sonoda, T.; Kang, H.; Tsumori, F.; Miura, H.; Funtai Oyobi Fummatsu, Y. Evaluation and analysis of distortion during MIM process of titanium alloy materials—2nd report. *J. Jpn. Soc. Powder Powder Metall.* **2012**, *59*, 272–277. [[CrossRef](#)]
27. Bideaux, J.-E.; Closuit, C.; Rodriguez-Arbaizar, M.; Carreno-Morelli, E. Metal injection moulding of Ti-Nb alloys for implant application. *Eur. Cells Mater.* **2011**, *22*, 32.
28. Åslund, C. Novel process for producing components in high alloyed stainless steels. In Proceedings of the Advances in Powder Metallurgy and Particulate Materials, Powder Met, San Diego, CA, USA, 17–20 May 2015; Volume 2, pp. 07.91–07.98.
29. Kearns, M.; Johnston, M.; Murray, K.; Davies, P.; Ryabinin, V.; Gonzalez, E. Studies on the effects of Nb on sintering and properties of MIM 440C made by prealloy and master alloy routes. In Proceedings of the International Conference on Powder Metallurgy and Particulate Materials, PowderMet, San Diego, CA, USA, 17–20 May 2015; p. 1134.
30. Liu, C.; Kong, X.; Wu, S.; Kuang, C. Research on powder injection molding of Ti6Al4V alloys for biomedical application. *Powder Metall. Technol.* **2018**, *36*, 217–222+229.
31. Cai, Y. Technology and application for titanium and its alloy powder injection molding. *Rare Met. Mater. Eng.* **2005**, *34*, 657.
32. Miura, H.; Shinozaki, R.; Virdhian, S.; Osada, T. Evaluation and analysis of distortion during MIM process of titanium alloy materials. *J. Jpn. Soc. Powder Powder Metall.* **2010**, *57*, 352–356.
33. Gross, M.; Motivans, L. Bimetallic MIM medical components Medical Device Materials. In Proceedings of the Materials and Processes for Medical Devices Conference, Anaheim, CA, USA, 8–10 September 2003; pp. 403–407.
34. Melli, V.; Rondelli, G.; Sandrini, E.; Altomare, L.; Bolelli, G.; Bonferroni, B.; Lusvarghi, L.; Cigada, A.; De Nardo, L. Metal injection molding as enabling technology for the production of metal prosthesis components: Electrochemical and in vitro characterization. *J. Biomed. Mater. Res. B Appl. Biomater.* **2013**, *101*, 1294–1301. [[CrossRef](#)] [[PubMed](#)]

35. Bockris, J.; Genshaw, M.; Brusic, V.; Wroblowa, H. The mechanism of the passivation of iron in neutral solutions: An ellipsometric and coulometric investigation. *Electrochim. Acta* **1971**, *16*, 1859–1894. [\[CrossRef\]](#)
36. Shaw, B. Corrosion-Resistant Powder Metallurgy Alloys. In *Powder Metal Technologies and Applications*; ASM International: Novelty, OH, USA, 1998; p. 7. [\[CrossRef\]](#)
37. Tandon, R.; Simmons, J.; Covino, B.; Russel, J. Mechanical and corrosion properties of nitrogen-alloyed stainless steels consolidated by MIM. *Int. J. Powder Metall.* **1998**, *34*, 47–54.
38. Castro, L.; Merino, S.; Levenfeld, B.; Varez, A.; Torralba, J.M. Mechanical properties and pitting corrosion behaviour of 316L stainless steel parts obtained by a modified metal injection moulding process. *J. Mater. Process. Technol.* **2003**, *143*, 397–402. [\[CrossRef\]](#)
39. He, H.; Li, Y.; Li, D. Effect of sintering temperature and atmosphere on corrosion behavior of MIM 316L stainless steel. *Adv. Mater. Res.* **2011**, *239*, 132–136. [\[CrossRef\]](#)
40. Varma, D.P.; Chidambaram, S.; Reddy, K.B.; Vijay, M.; Ravindranath, D.; Prasad, M.R. Comparison of galvanic corrosion potential of metal injection molded brackets to that of conventional metal brackets with nickel-titanium and copper nickel-titanium archwire combinations. *J. Contemp. Dent. Pract.* **2013**, *14*, 488–495.
41. Siargos, B.; Bradley, T.G.; Darabara, M.; Papadimitriou, G.; Zinelis, S. Galvanic corrosion of metal injection molded (MIM) and conventional brackets with nickel-titanium and copper-nickel-titanium archwires. *Angle Orthod.* **2007**, *77*, 355–360. [\[CrossRef\]](#)
42. Xu, Z.; Jia, C.; Kuang, C.; Qu, X.H. Fabrication and sintering behavior of high-nitrogen nickel-free stainless steels by metal injection molding. *Int. J. Miner. Metall. Mater.* **2010**, *17*, 423–428. [\[CrossRef\]](#)
43. Uggowitzer, P.; Bähre, W.; Wohlfromm, H. Nickel-free high nitrogen austenitic stainless steels produced by metal injection moulding. *Speidel M Mater. Sci. Forum* **1999**, *318*, 663–672. [\[CrossRef\]](#)
44. Baker, M. European Standards Developed in Support of the European Union Nickel Directive. *Met. Allergy* **2018**, 23–29.
45. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Establishing a European Chemicals Agency, amending Directive 1999/45/EC and Repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02006R1907-20140410> (accessed on 15 November 2023).
46. Substances of Very High Concern Identification. Available online: <https://echa.europa.eu/substances-of-very-high-concern-identification> (accessed on 15 November 2023).
47. Cui, D.; Qu, X.; Guo, P.; Li, K. Sintering optimization and solution annealing of high nitrogen nickel free austenitic stainless steels prepared by PIM. *Powder Metall.* **2010**, *53*, 91–95. [\[CrossRef\]](#)
48. Uggowitzer, P.; Bahre, W. Metal injection moulding of nickel-free stainless steels. *Speidel M Adv. Powder Metall. Part. Mater.* **1997**, *318*, 663–672.
49. Shashanka, R.; Chaira, D. Effects of nano-Y₂O₃ and sintering parameters on the fabrication of PM duplex and ferritic stainless steels. *Acta Metall. Sin.* **2016**, *29*, 58–71. [\[CrossRef\]](#)
50. Kuang, C.J.; Zhong, H.; Chen, D.; Kuang, X.; Li, Q.; Hao, Q. Development of powder metallurgy nickel free high nitrogen stainless steels. *Mater. Sci. Forum* **2010**, *638*, 1811–1813.
51. Kuroda, Y.; Komada, M.; Murakami, R.; Fukumoto, S.; Tsuchida, N.; Harada, Y.; Fukaura, K. Metal injection molding of nickel-free austenitic stainless-steels I—Manufacturing process. *Adv. Mater. Res.* **2007**, *26*, 15–18. [\[CrossRef\]](#)
52. Johnson, J.; Tan, L.; Suri, P.; German, R. Metal injection molding of multi-functional materials. *Am. Soc. Mech. Eng.* **2003**, *98*, 283–288.
53. Sonderegger, M.; Spruengli, B. Optimised sintering and heat treatment of the nickel-free high-nitrogen MIM-Steel X15CrMnMoN17-11-3. In Proceedings of the Euro PM 2006—Powder Metallurgy Congress and Exhibition, Ghent, Belgium, 23–25 October 2006; Volume 2, pp. 31–36.
54. Reclaru, L. Yesterday, today, and tomorrow ceramics, Ni-Cr and Co-Cr alloys in dental prosthetic application. *Clujul Med.* **2017**, *90*, 67–79.
55. Keong, T. Feedstock development for micro metal injection molding (μ -MIM). In Proceedings of the Euro International Powder Metallurgy Congress and Exhibition, Euro PM, Mannheim, Germany, 29 September–1 October 2008; Volume 2, pp. 317–323.
56. ASTM G48-11 (2020); Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution. ASTM International: West Conshohocken, PA, USA, 2020. [\[CrossRef\]](#)
57. Bockris, J.O.; Reddy, A.K.N.; Gamboa-Aldeco, M. Modern Electrochemistry. *Fundam. Electrodicts* **2000**, *2A*, 1140.
58. Pleskov, Y.V. The Rotating Disc Electrode. In *Studies in Soviet Science*; Halina, S., Wroblowa, B., Conway, E., Eds.; Consultants Bureau-New York and London, A Division of Plenum Publishing Corporation: New York, NY, USA, 1967; p. 402.
59. Koutecky, J.; Levich, V.G. The Use of a Rotating Disk Electrode in the Studies of Electrochemical Kinetics and Electrolytic Processes. *Zh. Fiz. Khim.* **1958**, *32*, 1565–1575.
60. Levich, V.G.; Tobias, C.W. Physicochemical Hydrodynamics. *J. Electrochem. Soc.* **1963**, *110*, 251. [\[CrossRef\]](#)
61. ASTM G3-14 (2019); Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing. Corrosion of Metals; Wear and Erosion. ASTM International: West Conshohocken, PA, USA, 2019. [\[CrossRef\]](#)
62. ASTM G5-14 (2021); Standard Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements. Corrosion of Metals; Wear and Erosion. ASTM International: West Conshohocken, PA, USA, 2021. [\[CrossRef\]](#)

63. ASTM G59-97 (2020); Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements. Corrosion of Metals; Wear and Erosion. ASTM International: West Conshohocken, PA, USA, 2020. [[CrossRef](#)]
64. ASTM G71-81 (2019); Standard Guide for Conducting and Evaluating Galvanic Corrosion Tests in Electrolytes. Corrosion of Metals; Wear and Erosion. ASTM International: West Conshohocken, PA, USA, 2019. [[CrossRef](#)]
65. EN 1811; Reference Test Method for Release of Nickel from All Post Assemblies Which Are Inserted into Pierced Parts of the Human Body and Articles Intended to Come into Direct and Prolonged Contact with the Skin. European Committee for Standardization: Bruxelles, Belgium, 2023; C/2023/1604 (2024-01-31) for Directive 1907/2006.
66. ASTM F746-87 (1999); Standard Test Method for Pitting or Crevice Corrosion of Metallic Surgical Implant Materials. Medical and Surgical Materials and Devices (I). ASTM International: West Conshohocken, PA, USA, 1999. [[CrossRef](#)]
67. ASTM E112-13 (2021); Standard Test Methods for Determining Average Grain Size; Metals-Mechanical Testing. Elevated and Low-temperature Tests; Metallography. ASTM International: West Conshohocken, PA, USA, 2021. [[CrossRef](#)]
68. Sanderow, H.I. High-Temperature Sintered Powder Metal Parts, SAE Technical Paper. *SAE Trans.* **1990**, *99*, 112–115.
69. ASTM G15-02 (2017); Standard Terminology Relating to Corrosion and Corrosion Testing. Corrosion of Metals; Wear and Erosion. ASTM International: West Conshohocken, PA, USA, 2017. [[CrossRef](#)]
70. ASTM F2229-02 (2021); Standard Specification for Wrought, Nitrogen Strengthened 23Mn-21Cr-1Mo Low-Nickel Stainless Steel Alloy Bar and Wire for Surgical Implants. Medical and Surgical Materials and Devices (I). ASTM International: West Conshohocken, PA, USA, 2021. [[CrossRef](#)]

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