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Mechanical and Electrochemical Characterization of Supersolidus Sintered Austenitic Stainless Steel (316 L)

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Abstract: The present study compares the mechanical properties and electrochemical behaviour of austenitic (AISI 316 L) stainless steel compacted at different pressures (200, 400 and 600 MPa), which are conventionally sintered at supersolidus temperature of 1,400°C. As expected, increase in compaction pressure (from 200 MPa) to 600 MPa has shown decreased shrinkage (from 7.3% to 4.2% radial and 5.5% to 3.4% axial, respectively) and increased densification (up to ~92%). Their electrochemical behaviour was investigated in 0.1 N H₂SO₄ solution by potentiodynamic polarization and electrochemical impedance spectroscopy. The mechanical properties (such as yield-, tensile- and transverse rupture strength) and electrochemical behaviour with pressure have been correlated with densification response and microstructure (pore type, volume and morphology). Highest densification (~92% theoretical) achieved at 600 MPa (compaction pressure) and 1,400°C (sintering temperature) resulted in excellent combination of tensile strength and ductility (456 ± 40 MPa and 25 ± 1.1% respectively), while showing lowest corrosion rate (0.1 mmpy or 4.7 mpy) due to the presence of isolated porosity in the sintered samples.

Keywords: austenitic stainless steel; compaction pressure; supersolidus sintering; densification; electrochemical behaviour

Introduction

Austenitic stainless steels (316 L) have been widely used in a variety of product forms for architectural, biomedical, industrial and nuclear applications due to its excellent corrosion and oxidation resistance, good strength (tensile

strength 500–600 MPa), excellent toughness (impact energy of 125 J at –200°C to 220 J at 90°C) and formability (strain at fracture > 30%) [1, 2]. Powder metallurgical (P/M) processing offers the advantage of low cost net-shaping with high material utilization (95%), relatively low-temperature processing and a more refined and homogeneous microstructure [3]. P/M stainless steels consolidated through solid-state sintering at relatively low temperatures suffer from poor mechanical and corrosion properties which are attributed to their inherent porosity [4–9]. The activated sintering routes (with pure elements like Al, Cu, Sn, etc.) adopted by researchers have shown limited improvement in the densification, while beyond certain amount of activator show significant swelling (because of transient nature of liquid phases) that results in secondary porosity [10]. Alternatively, addition of phosphides (10 mass%) and boron (0.4 mass%) to stainless steel resulted in 96% and 98% of theoretical density but exhibited poor mechanical properties due to the presence of brittle phase at grain boundaries [11–13].

Stainless steel powders are typically fabricated through atomization, which results in a single-phase prealloyed structure. Such prealloyed powders are amenable to consolidation at higher temperatures through supersolidus liquid phase sintering involving heating the compacts between the solidus and the liquidus temperatures [14,15]. The liquid forms inside the particles and spreads to the particle contacts, resulting in a capillary stress-induced pore filling and increased diffusion kinetics thereby enhancing densification. Panda et al. [16] reported the onset of melt formation for the prealloyed 316 L powder as 1,383°C based on differential scanning calorimetry results. Several researchers have compared the densification response, mechanical (tensile test and hardness) and electrochemical properties (through potentiodynamic polarization) of 316 L compacted at 600 MPa and sintered at 1,200°C (solid state) and 1,400°C (supersolidus) [17–19]. Recently Pandya et al. [20] investigated the effect of sintering temperature (1,200, 1,300 and 1,400°C) on electrochemical properties using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Availability of limited literature on the investigation of EIS studies of supersolidus sintered

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stainless steel samples require further investigations. Pore volume and morphology greatly influence the mechanical and electrochemical properties and can be controlled by varying compaction pressure or sintering temperature. P/M stainless steels are primarily selected for their corrosion resistance and physical properties. Nevertheless, for a large majority of applications, it is essential that they should offer reasonably good mechanical strength and ductility. Therefore, evaluation of the mechanical performance of sintered stainless steels is essential. Electrochemical tests were conducted to understand the corrosion behaviour (kinetics and mechanism) of the super-solidus sintered 316 L stainless steels. In the present study, an attempt has been made to correlate the mechanical (YS, TS, TRS and hardness) and electrochemical properties of austenitic stainless steel (AISI 316 L) to the pore volume and morphology by compacting at 200, 400 and 600 MPa and sintering at 1,400°C.

Experimental procedure

Prealloyed water atomized 316 L stainless steel powder (composition Fe–16.5Cr–12.9Ni–2.48Mo–0.93Si–0.21Mn–0.025C–0.008S–0.01P in wt.%, and average particle size ~45–50 µm) was supplied by Ametek Specialty Metals Products, PA, USA. The powder was uniaxially pressed at compaction pressures of 200, 400 and 600 MPa. Cylindrical pellets (of ~16 mm dia, and ~6–7 mm thick) were formed using a semi-automatic hydraulic press (model: CTM-100, supplier: Bluestar, India) with zinc

stearate as a die wall lubricant. Sintering was carried out in hydrogen atmosphere (dew point: –35°C) in a MoSi₂ heated horizontal tubular sintering furnace (model: OKAY 70T-7, supplier: Bysakh, Kolkata, India) at a constant heating rate of 5°C/min. The compacts were consolidated isothermally at 1,400°C for 1 h. Two intermediate isothermal holds of 15 min each at 600 and 900°C were provided to ensure uniform temperature distribution, delubrication/debinding and reduction of oxides, respectively. The thermal cycle for sintering is shown in Figure 1. The green and sintered densities were determined from dimensional (thickness, diameter) and weight measurements. The sinterability of compacts was determined through densification parameter (DP), which is expressed as [1]

$$\text{Densification parameter} = \frac{(\text{sintered density} - \text{green density})}{(\text{theoretical density} - \text{green density})} \quad (1)$$

For microstructural and electrochemical analyses, sintered samples were mirror polished using series of SiC emery papers of grades 220, 320, 500 and 1,000, followed by cloth polishing using a suspension of 0.3 and 0.05 µm alumina diluted with water, and then were ultrasonically cleaned (5–7 min) in acetone. The microstructure of the samples was captured using an optical microscope (model: DM2500, supplier: Leica Imaging System Ltd, Cambridge, UK). Marble's reagent (50 mL HCl and 25 mL saturated aqueous copper(II) sulphate) was used as an etching agent. Unetched metallographic samples were utilized to evaluate stereological parameters of the pore

Figure 1: Thermal cycle used for sintering samples at 1,400°C.

structure. Pore and pore circumference were measured using % Round Standard in Qnodels licensed software from Leica. For each sample, pore structure quantification was done on ten micrographs captured randomly. Grain size was measured using linear intercept method. The measurements were done by considering five micrographs captured at different portions of each sample at $500\times$ magnification and 7–10 lines (200 μm length) oriented in various directions on each micrograph. Bulk hardness of the samples was measured using a Vickers hardness tester (Leco V-100-C1) at 5 kgf load. The microhardness of the samples was measured using Vickers hardness tester (Bareiss VTP 6046 Bj07) at 0.1 kgf load. The reported values are the average of 20 indentations at different areas in each sample. The mechanical properties (yield strength, ultimate tensile strength, % elongation and transverse rupture strength [TRS]) were measured using flat tensile bars and transverse rupture bars pressed as per Metal Powder Industrial Federation (MPIF) standards [21]. Figure 2(a) and (b) shows the dimensions of tensile and transverse rupture bars as per MPIF and tensile and transverse rupture bars (before and after testing) used in the present study. The gauge length of 26 mm was used for testing the sintered samples at room temperature through universal testing machine (1195, INSTRON, UK, maximum load of 20 kN) at an initial strain rate of $3.3\times 10^{-4}/\text{s}$ (or

crosshead speed 0.5 mm/min). The TRS of the sample was calculated as follows [1]:

$$\text{TRS} = \frac{3PL}{2t^2w} \quad (2)$$

where TRS is the transverse rupture strength (N/mm^2), P is the force to rupture (N), L is the distance between the supporting rods (26 mm), t is the thickness of the specimen (mm), w is the width of the specimen (mm). To correlate the tensile properties with the microstructure, fractographs of the tensile tested samples obtained using scanning electron microscope (Zeiss Evo 50, Carl Zeiss SMT Ltd, and UK), at an accelerating voltage of 20 kV.

The electrochemical behaviour of the samples was studied in freely aerated 0.1 N H_2SO_4 solution ($\text{pH } 1.31 \pm 0.05$) at room temperature using Electrochemical System (model: VersaSTAT 3, supplier: Princeton Applied research). Prior to polarization, the polished samples were allowed to stabilize for 1 h in 0.1 N H_2SO_4 to obtain stable open circuit potential (OCP) as per ASTM F2129. Electrochemical tests were carried out in a flat corrosion cell (supplier: Accutrol Inc., USA) using a standard three-electrode configuration with platinum mesh as the counter electrode, Ag/AgCl saturated with KCl as reference electrode (+197 mV with respect to hydrogen electrode) and the sample as the working electrode. Potentiodynamic polarization tests were

Figure 2: (a) Dimensions of tensile and transverse rupture samples as per MPIF standards (b) actual samples used in the present study.

carried out from -250 mV versus OCP to $+1,600$ mV versus reference electrode at a scan rate of 0.5 mV/s. The critical parameters like corrosion potential (E_{corr}) and corrosion current (I_{corr}), passivation current density (I_{pass}), critical current density (I_{crit}), breakdown potential (E_b) were determined from the polarization curves. EIS measurements were performed at room temperature after 1 h exposure (stabilization) in test solution (0.1 N H_2SO_4) to obtain stable OCP. EIS measurements were carried out over a frequency range of 100 kHz to 1 Hz or 10^5 to 1 Hz at OCP using 10 mV amplitude sinusoidal voltage. The response at frequency less than 1 Hz was subject to noise resulting into very high relative standard errors. In order to analyse the impedance behaviour of sintered stainless steel samples, equivalent circuit (EC) fitting was obtained using Zsimpwin software. The fitting procedure was based upon the non-linear least squares method.

Results and discussion

Densification and microstructure of sintered 316 L stainless steel samples

The densification of conventionally sintered samples is shown in Table 1. The green density increased from $68\text{--}69\%$ to as high as $82\text{--}83\%$ relative theoretical as the compaction pressure increased from 200 to 600 MPa. During sintering, all the samples underwent shrinkage (axial and radial) which is observed to decrease with increase in the compaction pressure. This can be correlated to increase in green density or decrease in porosity of samples with increase in the compaction pressure. Increase in compaction pressure (from 200 to 600 MPa) resulted in $\sim 42\%$ decrease in radial shrinkage and $\sim 38\%$ decrease in axial shrinkage. In all the samples, the radial shrinkage is more than that of longitudinal or axial shrinkage. This can be attributed to the fact that during compaction, the pores get elongated and become ellipsoid with its long axis perpendicular to the pressing direction. The curvature in transverse direction tends to

get rounded, which activates sintering due to curvature effect in comparison to that of planar surface existing along axial direction.

Optical micrographs of conventionally sintered samples (un-etched and etched) are shown in Figure 3. From the micrographs it is evident that the porosity level was higher in samples compacted at 200 MPa ($\sim 16\%$ by volume) and decreased (to 8% by volume) with increase in compaction pressure to 600 MPa, Figure 3a. This correlates with the densification results shown in Table 1. The microstructures revealed the presence of almost isolated pores (Figure 3b) with qualitatively larger inter-pore distance in samples compacted at 600 MPa and open connected ($67\text{--}70\%$) pores at near grain boundaries (intergranular) and few isolated ($30\text{--}33\%$) pores (intra-granular) in samples compacted at 200 and 400 MPa. Xylene impregnation method was used to determine the fraction of interconnected and isolated pores. The average grain size of the sintered samples was observed to be almost similar, i. e. 27 ± 2.6 , 27.5 ± 2.7 and 28 ± 2.9 μm , for samples compacted at 200 , 400 and 600 MPa, respectively, and sintered at $1,400^\circ\text{C}$. The average grain size slightly increased with increase in sintered density or decrease in porosity attributed to higher amount of break-away of grain boundaries from pores.

Unetched micrographs shown in Figure 3(a) were utilized to evaluate stereological parameters of the pore structure such as pore size (by measuring pore surface area) and pore perimeter. Pore shape factor is calculated using pore surface area (A in μm^2), and its circumference in the plane of analysis (P in μm), as follows [22]:

$$F = \frac{4\pi A}{P^2} \quad (3)$$

Pore shape factor (F) determines profile irregularity of a pore. The shape factor of 1 represents a circular pore in the plane of analysis and as the number decreases from 1 , the elongation and degree of irregularity increases.

Pore shape factor and pore area distributions of 316 L are shown in Figure 4. From the pore shape factor distribution in Figure 4(a), it can be observed that samples

Table 1: Effect of compaction pressure on densification response of 316 L stainless steel sintered at $1,400^\circ\text{C}$.

Compaction pressure (MPa)	Green density (g/cm^3)	Sintered density, g/cm^3 (%th density)	Radial shrinkage (%)	Axial shrinkage (%)	Densification parameter
200	5.52 ± 0.06	6.71 ± 0.06 (84%)	7.26 ± 0.04	5.47 ± 0.09	0.48 ± 0.01
400	6.22 ± 0.01	7.06 ± 0.01 (88%)	4.39 ± 0.01	3.84 ± 0.1	0.48 ± 0.005
600	6.58 ± 0.03	7.33 ± 0.03 (92%)	4.23 ± 0.01	3.37 ± 0.06	0.53 ± 0.01

Figure 3: Optical micrographs of un-etched (a–c) and etched (d–f) 316 L stainless steel compacted at different pressures and sintered at 1,400°C.

compacted at 200 and 400 MPa exhibited wider distribution and higher amount of irregular pores (~50–55% distribution lies in the shape factor of 0.1–0.6), while samples compacted at 600 MPa exhibited narrow

distribution and less irregular pores (~80% of distribution lies in the shape factor of 0.6–0.9). From Figure 4(b), it is clear that amount of rounded pores increased from ~10% to ~22% with increase in compaction pressure from

Figure 4: Comparison of (a) pore shape factor distribution (b) pore area distribution of 316 L samples compacted at different pressures and sintered at 1,400°C.

200 to 600 MPa. However, the maximum pore shape factor attained was almost close in all samples approaching a value ~ 0.8 .

A relative measure of densification was obtained through DP (Table 1) providing relative degree of compaction with density being normalized with respect to green density (as per the eq. (1) i.e. the ratio of reduction in porosity during sintering to initial porosity after compaction). The sintered density was observed to increase from 84% to as high as 92% relative theoretical and DP increased from 0.48 to 0.53 with increase in compaction pressure from 200 to 600 MPa, respectively. The higher residual strain in samples compacted at 600 MPa contributed to an initially faster sintering rate and correspondingly resulted in higher densification [3]. DP is a better indicator of the sinterability, as it takes care of the variation in the compact green density as well. Panda et al. [16] reported that 316 L samples sintered at solidus temperature (1,200°C) do not exhibit significant densification ($DP \leq 0.05$). The prealloyed powders themselves undergo partial melting during supersolidus sintering [15]. The densification enhancement at supersolidus sintering temperature (1,400°C) is attributed to increased diffusivity due to melt formation preferentially at grain boundaries. Melt formation at the intergranular region (composition varies) was confirmed by elemental analysis (line analysis). This melt formation enhances densification through capillary-induced pore filling and grain rearrangement [23]. Comparison of densification response of solidus and supersolidus sintered 316 L (conventional)

was reported in earlier publications [16, 18–20]. Sintered density (600 MPa compaction pressure) was observed to increase from 82.4–85.8% to 87.5–89.6% relative theoretical with increase in sintering temperature from 1,200°C (solidus) to 1,400°C (supersolidus). The sinter density obtained in this study is higher than that reported by other researchers under similar conditions i.e. 600 MPa, 1,400°C [16–20]. Energy dispersive spectroscopy analysis of 316 L compacted at 600 MPa and sintered at 1,400°C is presented in Figure 5, confirming the absence of oxidation during sintering, and presence of constituting elements of 316 L.

Mechanical properties of sintered 316 L stainless steel samples

Table 2 shows the effect of compaction pressure on the bulk and micro-hardness, strength and ductility of conventionally sintered 316 L stainless steels. The bulk hardness (HV_5) of the sintered compacts increased from 119 ± 5 (at 200 MPa) to 142 ± 3 (at 400 MPa) and 159 ± 4 (600 MPa) with increase in compaction pressure. The hardness values obtained in this study are higher than that reported by other researchers under similar conditions [16–18, 20]. The micro-hardness of sintered compacts was similar at all compaction pressures (of 200, 400 and 600 MPa) processed at all compaction pressures and elicited high standard deviation

Figure 5: EDS analysis of 316 L compacted at 600 MPa and sintered at 1,400°C.

Table 2: Mechanical properties of 316 L stainless steel compacted at different pressures and sintered at 1,400°C.

Compaction pressure (MPa)	Bulk hardness (HV ₅)	Micro-hardness (HV _{0.1})	Strength (MPa)			Elongation (%)
			YS*	UTS*	TRS*	
200	119 ± 5	251 ± 42	135 ± 3	251 ± 15	818 ± 19	14 ± 0.2
400	142 ± 3	273 ± 37	182 ± 1	362 ± 7	912 ± 11	21 ± 0.8
600	159 ± 4	286 ± 30	224 ± 26	456 ± 40	1,003 ± 15	25 ± 1.1
Wrought 316 L ¹	220 max	—	172	483	—	30

*YS: Yield strength; UTS: ultimate tensile strength; TRS: transverse rupture strength. ¹ASTM A479 (specification for annealed bar), A167–A240 (specification for annealed plate).

(~10–13%) due to the presence of porosity. In all the samples, lower hardness values were obtained in the vicinity of pores, whereas higher hardness values were obtained at pore free or fully dense regions.

Stress–strain curve of as-sintered tensile samples, at green-compaction pressures of 200, 400 and 600 MPa, is shown in Figure 6. With an increase in compaction pressure from 200 to 600 MPa, YS increased from 135 to

Figure 6: Tensile stress–strain curves of 316 L stainless steel compacted at different pressures and sintered at 1,400°C.

224 MPa (~66% improvement), UTS increased from 251 to 456 MPa (~82% improvement) and TRS increased from 818 to 1,003 MPa (~23% improvement), which can be directly attributed to the higher sintered densification (~92% relative theoretical density) and narrow pore shape and pore area distributions (Figure 4) of 600 MPa samples. Samples compacted at 600 MPa resulted in excellent combination of tensile strength and % elongation (456 ± 40 MPa, $25 \pm 1.1\%$) which are comparable to wrought 316 L [24]. The strength obtained is higher than that obtained by other researchers under similar conditions [17, 20]. Poor strength values of samples compacted at 200 and 400 MPa can be attributed to higher pore volume (16% and 12%, respectively) and irregular pores (Figures 3 and 4) which resulted in poor load bearing capacity and more stress concentration. Poor work hardening, easy pore coalescence and crack initiation have resulted in relatively lower ductility for samples, which are compacted at 200 and 400 MPa [3]. Several researchers have reported that irregular pore structures decrease the strength of P/M parts and that the ductility decreases with increase in porosity [16, 17, 20, 25, 26]. The fractographs depicted in Figure 7 revealed a cup and cone fracture for all samples which is indicative of rupture of material after a considerable amount of plastic deformation as a result of shear forces. There was no evidence of cleavage planes or decohesion planes. Similar ductile fracture behaviour has been reported by several researchers for supersolidus sintered 316 L stainless steel [16, 17, 20]. Presence of voids or cavities at matrix–pore interfaces indicates that the fracture nucleation, growth and crack propagation occurred at near pores.

Electrochemical properties of sintered 316 L stainless steel samples

Potentiodynamic polarization

Potentiodynamic polarization curves of 316 L samples compacted at different pressures and sintered at 1,400°C are shown in Figure 8. Samples compacted at 600 MPa showed slightly more positive OCP E_{corr} (–261 mV) value which indicates that the oxide film formed on 600 MPa samples is more effective on resisting the anodic dissolution, i. e. noble behaviour than that of 200 and 400 MPa samples. All samples showed passivity over a wide range of potential (0–0.92 V). The corrosion current (I_{corr}) was determined geometrically by using the corrosion potential and the Tafel region slopes (cathodic and anodic) of potentiodynamic plot. For the sample compacted at 600 MPa and sintered at 1,400°C, E_{corr} and the cathodic slope were used to calculate I_{corr} [27,28] as the anodic slope could not be determined due to the onset of passivation. The corrosion rate was calculated using first Stern method and is expressed as follows [29]:

$$\text{Corrosion rate (mmpy)} = 3268 \frac{e}{\rho} I_{\text{corr}} \quad (4)$$

where e is the equivalent weight (g), ρ is the density of the material (g/cm^3), I_{corr} is the corrosion current (A/cm^2).

Potentiodynamic polarization parameters of 316 L stainless steel compacted at different pressures and sintered at 1,400°C are presented in Table 3. Samples compacted at

Figure 7: Fractographs of 316 L stainless steel tensile tested samples compacted at (a) 200 MPa, (b) 400 MPa, (c) 600 MPa and sintered at 1,400°C.

600 MPa showed a much lower I_{crit} ($8.28 \mu\text{A}/\text{cm}^2$, two orders lower than that of 200 MPa), I_{pass} ($6.38 \mu\text{A}/\text{cm}^2$, ~30 times lower than that of 200 MPa) and I_{corr} value (~15 times lower than that of 200 MPa) resulted in better passivation and low corrosion rate (0.12 mmpy). Similar observations on the effect of porosity (by varying sintering temperature) on the I_{crit} and I_{pass} have been reported by various authors as well [18–20, 30, 31]. The corrosion rate is lower than that obtained by various researchers under similar conditions [18–20, 31] and it is close to that of wrought 316 L [32, 33]. The critical current density (I_{crit}) provides insights on nucleation and growth of passive film and passivation current density (I_{pass}) assesses the nature of the passive film formed. Lower the I_{crit} , the easier it is to passivate a material or to remain passive. A low I_{pass} implies slower diffusion of chromium through the passive film which is indicative of better corrosion resistance.

Since the grain size of all samples is similar (~27 µm), presence of open porosity (surface) in case of samples

compactd at 200 and 400 MPa resulted in higher corrosion rate due to easy diffusion of oxygen through available pores and enhanced surface area exposed to corrosive electrolyte, which prevents the passivity within the pores. A crevice corrosion mechanism within the intrinsic pores of the material could be the cause of the higher corrosion rate [34]. While higher compaction pressure leads to reduced surface porosity and specific surface area, it lowers interior corrosion through pore closure. Blockage of the electrolyte penetration has shown to decrease the corrosion kinetics when the porosity of sintered stainless steels diminishes, since active area develops an adherent and homogeneous oxide film [34]. Moreover, it can be clearly observed from Figure 9 that localized corrosion at more number of junctions and along grain boundaries in case of samples compacted at 200 and 400 MPa while samples compacted at 600 MPa showed substantially less number of junctions. In all samples, metal dissolution occurred primarily in the

Figure 8: Potentiodynamic polarization curves of 316 L samples compacted at different pressures and sintered at 1,400°C.

Table 3: Potentiodynamic polarization parameters of 316 L compacted at different pressures and sintered at 1,400°C.

Compaction pressure (MPa)	E_{corr} (mV)	I_{crit} ($\mu\text{A}/\text{cm}^2$)	I_{pass} ($\mu\text{A}/\text{cm}^2$)	E_b (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mppy)
200	-294	829	184	936	157	2.13
400	-269	65	36	918	45	0.58
600	-261	8.3	6.4	915	10	0.12
Wrought [30]	-300	30	6.8	800	17	0.19

interior of the material. Similar behaviour has been reported by other researchers [20, 35, 36]. The passivity was found to be broken in the order of decreasing sintered density, with the wrought samples showing the breakdown at the least anodic potential. The current densities were found to approach the same order of magnitude at substantially higher anodic potential (923 ± 11 mV). Presence of Mo (2.48 wt.%) has restricted pitting (as seen in Figure 9). In addition, lower concentration of electrolyte could also account for the absence of pitting.

EIS

The Nyquist and the Bode plots acquired from impedance measurements are shown in Figures 10(a) and (b). The EIS results were analysed quantitatively, and the EC models were applied, as shown in Figure 11 (circuit with two hierarchical parallel RC loops in series with the resistance

of the electrolyte). The high-frequency arc formed in a frequency range from 10^3 Hz to 10^5 Hz is introduced by the large internal resistance of the reference electrode which induces capacitive high-frequency phase shift in impedance measurement [37] and its influence on the whole impedance is negligible. The second arc appeared at frequencies lower than 10^3 Hz is due to the interfacial reaction including two processes with the similar and inseparable time constants. These processes include the effect of oxide layer as a protective barrier and the redox reaction on material surface. The physical meaning of each element in the EC is explained as follows: the loop $R_{\text{ct}}-C_{\text{dl}}$ represents the charge transfer process, and it's composed by the charge transfer resistance (R_{ct}) in parallel with the double layer capacitance (C_{dl}); loop R_p-CPE_f is related with a redox transformation of the corrosion products that occurs on the surface of the passive film; the resistance that appears at very high frequencies corresponds to the resistance of the solution or electrolyte (R_s). The film

Figure 9: SEM micrographs of 316 L samples compacted at (a) 200 MPa, (b) 400 MPa, (c) 600 MPa and sintered at 1,400°C after potentiodynamic testing.

Figure 10: (a) Nyquist plot and (b) Bode magnitude plot for 316 L compacted at different pressures and sintered at 1,400°C.

Figure 11: Equivalent circuit model to represent the corrosion mechanism of 316 L.

capacitance usually deviates from pure capacitance presenting depressed semi-circles in the Nyquist plots called dispersion effect which may be caused by the roughness of electrode surface or non-uniform distribution of the current density on the electrode surface [38,39]. Hence, the capacitance was replaced by a constant-phase element (CPE). Several researchers used this two time constant circuit to simulate the electrochemical behaviour of stainless steels in non-aggressive environments [20, 40–42]. The values of the parameters obtained with the fitting procedure are reported in Table 4.

Oxide film capacitance (CPE_f) and capacitance of double layer (C_{dl}) decreased with increase in compaction pressure. Since pores make the real surface exposed to corrosion higher than that directly measured (apparent surface area), the obtained C_{dl} values (Table 4) are higher than typical capacitance ($10 \mu\text{F}/\text{cm}^2$) corresponding to a charge transfer process. The real area that suffers the attack in P/M steels i. e. active area factor (AAF) can be calculated by dividing C_{dl} (Table 4) by $10 \mu\text{F}/\text{cm}^2$ [42]. AAF decreased from 27 to 4 as the compaction pressure

increased from 200 to 600 MPa and it is closely related to the volume of the porosity of samples. The obtained AAF values are comparable to those assumed by Fedrizzi et al. (10–100 times) depending on the open porosity and pore shape [9]. CPE_f is a measure of the penetration performance of water or other ions into oxide film. Lower the CPE_f , higher will be the barrier ability of film against penetration. The sum resistance (the resistance of real part of Nyquist plots at the lowest frequency) of film resistance and charge transfer resistance dictates the corrosion resistance performance of sample. The values obtained for Polarization resistance (R_p) from the EIS spectra are about one order of magnitude lower than those obtained for charge transfer resistance (R_{ct}). Higher the R_p , the lower the ion release, subsequently lower corrosion rate. Higher the charge transfer resistance (R_{ct}), higher the protective ability of passive layer and low ion transfer rate and hence results in higher corrosion resistance. The values of R_p and R_{ct} of 600 MPa are about four and six times more than that of 200 MPa samples (212 vs. 49 Ωcm^2 for R_p , and 3,421 and

Table 4: Electrochemical impedance spectroscopy parameters obtained for 316 L compacted at different pressures and sintered at 1,400°C.

Compaction pressure	R_{solution} (Ωcm^2)	$CPE_{\text{oxide film}}$ ($\mu\text{F}/\text{cm}^2$)	$R_{\text{polarization}}$ (Ωcm^2)	$C_{\text{double layer}}$ ($\mu\text{F}/\text{cm}^2$)	$R_{\text{charge transfer}}$ (Ωcm^2)
200	10.46 (1.99%)*	127.2 (5.65%)*	48.54 (10.36%)*	268.7 (5.98%)*	527 (11.26%)*
400	9.73 (1.82%)*	40.76 (3.02%)*	201.3 (11.88%)*	42.7 (7.53%)*	1,387 (6.7%)*
600	9.61 (1.59%)*	37.16 (2.78%)*	211.7 (13.14%)*	37.73 (6.03%)*	3,421 (8.09%)*

*Relative standard errors are mentioned in parenthesis.

527 $\Omega \text{ cm}^2$, respectively, for R_{ct} , see Table 4), which indicates lower metal dissolution and higher passive behaviour (2.12 vs. 0.12 mmpy for I_{corr} , see Table 3) attributed to less pore volume (8%) and absence of surface or interconnected pores.

Conclusions

In summary, all the sintered stainless steel (AISI 316 L) pellets underwent shrinkage which decreased as compaction pressure increased. In all samples, the radial shrinkage was observed to be more (~up to 1.8%) than that of axial shrinkage. Pore volume, inter-pore spacing, morphology (shape and size) and nature (open or isolated) greatly affected the mechanical properties (strength, ductility and hardness) and kinetics of corrosion. The samples compacted at 600 MPa and sintered at 1,400°C (supersolidus) showed highest densification (92% of theoretical density). Excellent combination of strength and ductility (456 ± 40 MPa, $25 \pm 1.1\%$, respectively) and higher hardness (163 HV₅) attributed to substantially lower pore volume (8%) and rounded pores in sample compacted at 600 MPa. Higher polarization and charge transfer resistance shown by 600 MPa compacted and sintered sample resulted in good corrosion resistance (corrosion rate 0.12 mmpy or 4.7 mpy) due to the absence of interconnected pores in the sintered samples.

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