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Effect of Zr, Nb and Ti Additions on Injection Molded 316L Stainless Steel : Microstructural, Mechanical Properties and Corrosion Resistance

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Abstract : The objective of this research is to investigate the effect of Zr, Nb and Ti additions on microstructural, mechanical and electrochemical properties of injection molded 316L stainless steel. The amount of additive powder plays a role in determining the sintered microstructure and all properties. In this study, 316L stainless steel powders used with the elemental Zr, Nb and Ti powders. The binders were completely removed from molded components by solvent and thermal debinding. The debinded samples were sintered at different temperature for 60 min. at different temperatures. Mechanical property, microstructural characterization and electrochemical property of the sintered samples were performed using tensile testing, hardness, optical, scanning electron microscopy and electrochemical experiments. Results of study showed that sintered 316L and 316L with additive powder samples exhibited high mechanical and corrosion properties in a physiological environment.

Introduction

Powder injection molding (PIM) is a manufacturing technology for the net-shape production of small, intricate, and precise metallic and ceramic parts and components. The PIM process includes mixing of powders with a binder to produce a feedstock; injection molding to form a green part with the desired shape by making the feedstock flow into and fill a mold under pressure; debinding to form a brown part by removing the binder components, and finally sintering to near full density. The process overcomes the shape limitation of traditional powder compaction, the cost of machining, the productivity limits of isostatic pressing and slip casting, and the defect and tolerance limitations of conventional casting [1, 2].

In recent years, the interest in PIM for stainless steel alloys such as 316L, 17-4PH and 430 and their alloy parts for general use (household, automotive, dental, biomedical, military and aerospace) has dramatically increased [3], as evidenced by the number of scientific papers and successful use-oriented developments. Stainless steel alloys have been investigated due to their attractive properties, such as specific strength with good ductility, excellent surface properties, corrosion resistance and average density compared to other materials [2]. 316L alloys in stainless steel family have an average density, relatively high strength and excellent corrosion resistance in many media [4]. These materials can be easily produced by conventional powder metallurgy processing, but a major problem to be overcome in the conventional powder processing is the oxide film and residual radical elements such as C, O and N [5]. Oxides, nitrides and sulfur on surfaces of powder prevents to high densification at sintering stages. These problems form a large barrier for sintering behaviors and the final properties of 316L alloys. In general, 316L powder can be sintered by solid-state sintering technique. In this technique, surface and volume diffusion promotes high densification. Some elemental additives such as Zr, Ti and Nb in starting 316L powder can trap oxides on powder surfaces. As a result of this, it may be possible high performance for final sintered parts. Earlier investigations on injected molded 316L stainless steel focused on the effect of powder characteristics, the development of a binder system and debinding properties, sintering conditions,

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residual carbon and oxygen content on microstructure and small additives such as Zr, Ti and B to enhance sintering behavior and mechanical properties [5-8]

The present work investigates the effect of Zr, Nb and Ti additions microstructural and mechanical properties of injection molded 316L stainless steels. Metallographic techniques were employed for the sintered tensile bars to investigate the microstructural development. Tensile strength and hardness of the sintered products were evaluated to show the effects of final properties. Morphology of powders and fracture of sintered samples were also examined using SEM techniques. The sintered samples were characterized for their corrosion resistance in an acid solution (0.5M H_2SO_4) using potentiodynamic polarization.

Experimental Procedures

In this research, gas atomized 316L stainless steel powders (Fe-17Cr-12Ni-2.5Mo-1Si-2Mn-0.03C-0.045P-0.003S) provided by Osprey Metals Ldt. was used to prepare the samples. The Zr, Nb and Ti powder was obtained from Alfa Aesar. Particle size distributions of all powder were determined on Malvern Mastersizer equipment and given in Table 1. Morphology of the 316L powder was examined using scanning electron microscopy (JEOL- JSM 6335F). The gas atomized 316L stainless steel powder is spherical in shape and additive powder is irregular in shape.

Table 1. Powder characteristic of 316L, Zr, Nb and Ti powder

Item	316L	Zr	Nb	Ti
Vendor	Osprey Metals	Alfa Aesar	Alfa Aesar	Alfa Aesar
Shape	Spherical	Irregular	Irregular	Irregular
Particle size				
D_{10}	4.41	1.95	3.01	2.35
D_{50}	12.01	6.97	8.21	7.81
D_{90}	27.70	26.72	25.62	30.2
Purity, %	--	99.9	99.9	99.9

The amount of additives was given 0.25, 0.50 and 0.75 wt% in starting mixture and each mixture was blended in a Turbula mixer for five hours. A multiple-component binder system consisting of paraffin wax, polypropylene, carnauba wax, and stearic acid was employed. The powder loading in this mixture was 62.5 vol%. These feedstocks were injected using a 12.5 MPa tailor-designed injection molding machine to produce tensile (MPIF 50) test specimens. The melting temperature was 175ºC, the mold temperature was kept at 35ºC.

Debinding was performed in a two-step solvent/thermal operation. Green parts were solvent debound at 60ºC for 5 h in heptane, followed by thermal debinding step at slow heating rate of 600ºC for 1 h and pre-sintered at 4 ºC/min to 900ºC for 1 h in high purity hydrogen atmosphere. Sintering of all samples was performed in an atmosphere-controlled high temperature furnace. The sintering cycle was as follows: samples were heated to 1100ºC at a rate of 10 ºC/min and held at 1100ºC for 5 min., then the samples were heated to sintering temperatures of 1250ºC and 1350ºC at a rate of 5 ºC/min and they were held at sintering temperature for 60 min. in high purity hydrogen atmosphere.

The densities of the sintered samples were measured by means of the Archimedes water-immersion method. For metallographic examination, samples were cut from the center of the each sintered tensile test bar. All tensile tests were performed using Zwick 2010 mechanical tester at a constant crosshead speed of 1 mm/min. The hardness tests were performed using an Instron-Wolpert Dia Testor 7551 at HRA scale. The fracture surfaces were examined using a scanning electron microscope. At least three samples were tested under the same conditions for the reliability of the results.

For electrochemical evaluation, the cylindrical samples were polished to mirror finish in alcohol. The potentiodynamic scans were conducted using a flat cell, supplied by Gamry Instruments at room temperature. A standard three-electrode (reference, counter and working) technique was used for the measurement. The reference electrode used for the present experiment was saturated calomel

electrode and the sintered alloy was chosen as the working electrode. The exposed area of the sintered sample to the solution was 8.03 mm^2. The electrochemical experiments were performed using a PC controlled Gamry Echem Analyst system software. Prior to the polarization test, each sample was stabilized for about the solution to get a stable open circuit potential (OCP). The potentiodynamic polarization tests were conducted minimum of three times at a constant scan rate of 1 mVs−1 in freely aerated 0.5 M H2SO4. The potentiodynamic scan of sample was given in graphical form (voltage versus current density). The Tafel slopes were established from the active region of the corresponding anodic and cathodic curves. The critical parameters like corrosion potential (*E*corr), corrosion current (*I*corr) and corrosion rate were evaluated from the polarization curves.

Results and Discussion

The effect of sintering temperature and additions on the sintered density of 316L stainless steel is shown in Fig. 1. Fig. 1 shows that at sintering temperature 1250ºC, 1350ºC and sintering time 60 min., 316L samples attained a maximum density of 7.0 and 7.2, respectively. In 0.25, 0.50 and 0.75 wt% Nb added samples at sintering temperature 1250 ºC, 1350ºC and sintering time 60 min., attained a maximum density of 7.0 to 7.2, 7.1 to 7.3 and 7.1 to 7.4, respectively. In 0.25, 0.50 and 0.75 wt% Zr added samples at sintering temperature 1250ºC, 1350ºC and sintering time 60 min., attained a maximum density of 7.2 to 7.3, 7.2 to 7.4 and 7.3 to 7.4, respectively. In 0.25, 0.50 and 0.75 wt% Ti added samples at sintering temperature 1250ºC, 1350ºC and sintering time 60 min., attained a maximum density of 6.9 to 7.2, 7.0 to 7.3 and 7.0 to 7.1, respectively. The densities of all samples were increased with increasing sintering temperature and Nb and Zr additions. However, Ti additions caused a decrease in the density of samples. This result shows that the two types of additions improve the density of samples.

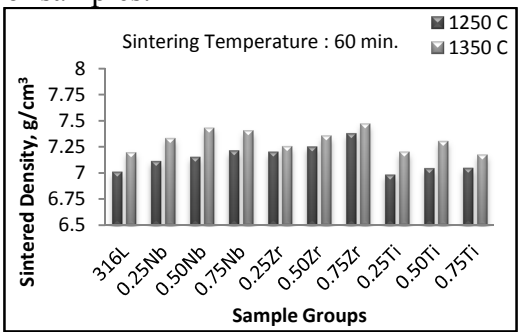


Fig. 1. Effect of sintering temperature and three type addition on the sintered density of injection molded 316L stainless steel

Fig. 2. shows the optical micrographs of 316L samples with and without additions sintered for 60 min. at 1250ºC and 1350ºC. From Fig. 2 it is evident that 316L stainless steels sintered for 1350ºC have significantly lower porosity compared to the 1250ºC sintered samples. Sintering results in improved sintered density in all straight 316L as well as 316L-additions samples. Ti added samples present lower density (Fig. 1) than that of 316L stainless steel at all sintering temperatures, for two reasons. The first reason is the lower density of the additions that reduces the density of the sintered samples. The second reason is that added particles impede the sintering process.

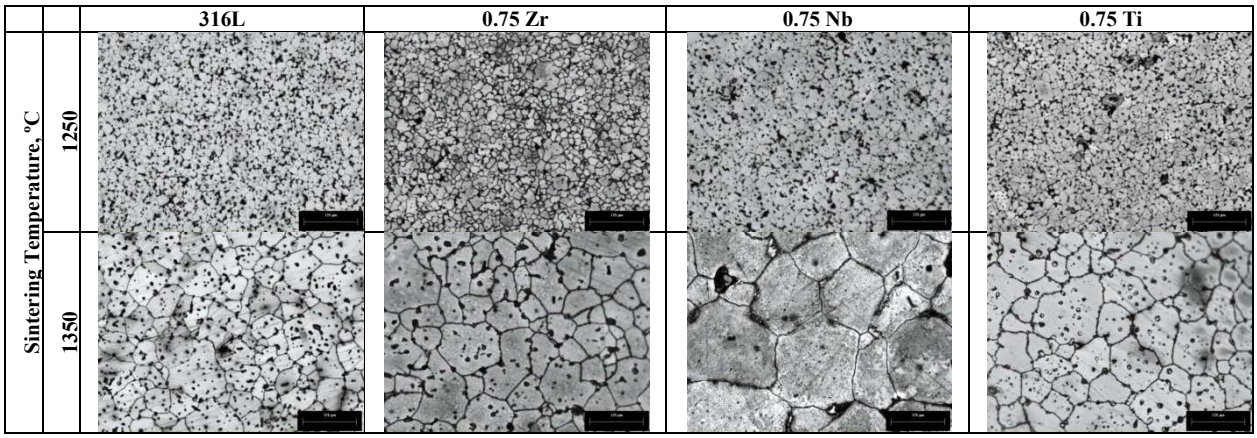


Fig. 2. Optical micrographs of 316L and 316L-additions samples sintered at 1250ºC and 1350ºC

The effect of sintering temperature and three type additions on the mechanical properties of 316L stainless steel is shown in Fig. 3. 316L stainless steel presents good mechanical properties, especially tensile strength (Fig. 3a), lower than that of added samples. The ultimate tensile strength was increased with sintering temperature. Thus, pores are closed and densities increased at high sintering temperatures. In added samples, ultimate tensile strength was increased compared to base samples, but in more additions samples (Zr 0.75 %), ultimate tensile strength was decreased. The effect of sintering temperature and additions on the hardness of 316L stainless steel is shown in Fig. 3b. The hardness of 316L stainless steels samples sintered for 1350ºC was higher than those sintered at 1250ºC. The 316L with Nb and Zr addition also shows an increase in hardness. This can be rationalized in terms of the enhanced hardness in 316L-additions alloys.

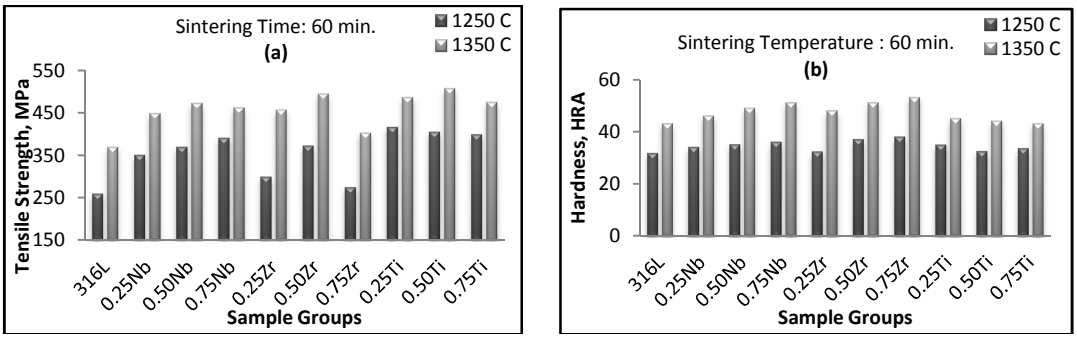


Fig. 3. Effect of sintering temperature and three type additions on (a) ultimate tensile strength and (b) hardness of injection molded 316L stainless steel

Fig. 4. shows the fracture surfaces of the samples. At low sintering temperatures, main fracture mode is the separation of particles and necking areas where bonding between particles took place during sintering. From Fig. 4, they are evident that straight 316L compacts show dimpled morphology, which is indicative of ductile fracture. In added samples, fracture mode from dimpled to intergranular mode.

Fig. 5. shows the extrapolation of the Tafel curves the corrosion potential, Ecorr (measured relative to SCE), Tafel slopes in the anodic and cathodic region and corrosion current density (icorr) were determined. Irrespective of the additive and sintering temperature are a significant improvement in the corrosion resistance for the sintered samples. This can be attributed to the enhanced densification achieved by the 1350ºC sintered samples. In additions, Zr Nb and Ti additives improved the corrosion resistance. The addition of 0.75 wt.% Ti to 316L stainless steels more improves the corrosion resistance in both sintering temperature.

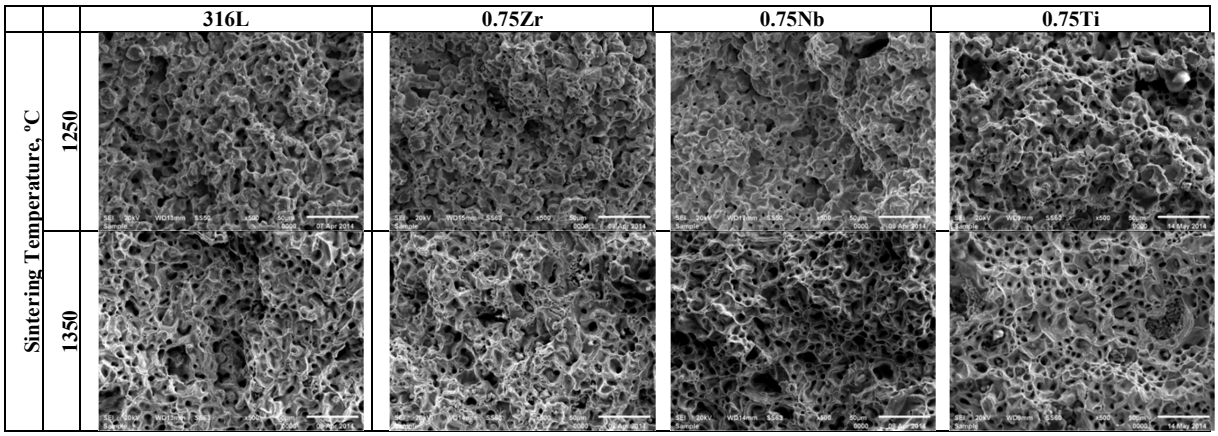


Fig. 4. SEM fractographs of 316L and 316L-additions samples sintered at 1250ºC and 1350ºC

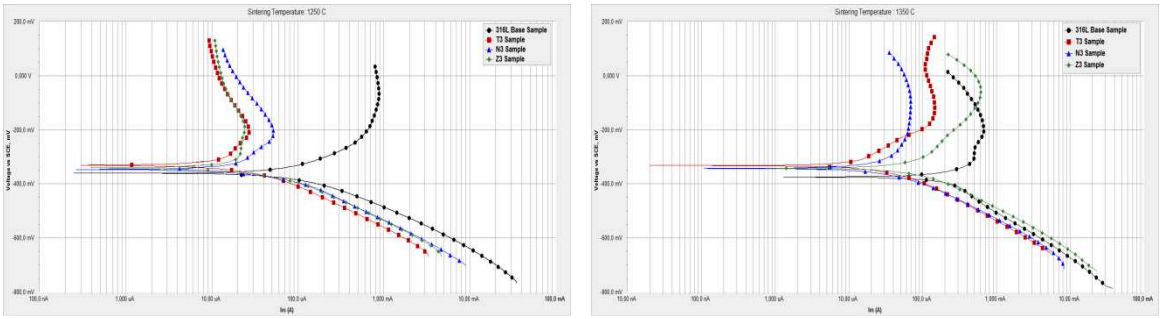


Fig. 5 Tafel curves for the 316L and 316L- additions samples sintered at 1250ºC and 1350ºC

Summary

The present study investigates the effect of Zr, Nb and Ti addition and sintering temperature on thesintered density, mechanical and corrosion properties of injection molded 316L stainless steel. The overall mechanical and corrosion performance of injection molded 316L stainless steel and 316L with Zr, Nb and Ti additions correspondingly improves with increase in the sintering temperature.

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