Corrosion Characterization of AISI 304 Stainless Steel Filter

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Abstract: Pre-sintering for removal of lubricants is one of the most important steps in processing of powder metallurgy materials to achieve corrosion resistance. This is often the most neglected step in the sintering process. Incomplete removal of these organic compounds may result in sensitization of sintered parts. The aim of this study is to investigate the effect of lubricant removal process on the corrosion resistance of sintered AISI 304 L stainless steel filters. Pre-sintering was carried out at 450° C and sintering at 1150° C. As lubricant, 1% wax was used. The corrosion resistance of sintered samples was evaluated by polarization and tests, optical and scanning electron microscopy. The results showed that lubricant removal was not complete and during sintering sensitization of the stainless steel occurred decreasing the localized corrosion resistance of the stainless steel.

Introduction

Austenitic stainless steels of the 300 series represent the great majority of stainless steels used in the area of powder metallurgy, with AISI 316 L being the most used commercial alloy[1]. Stainless steels can be sintered under hydrogen atmosphere where metal oxides are reduced to form H_2O, CO or CO_2[2]. A volatile silicon oxide is formed when Si is present in the alloy. The main disadvantage in the use of H_2 as sintering atmosphere is its high cost[3]. The most commonly used commercial atmosphere for sintering austenitic steels is H_2 (75%) and N_2 (25%). In this type of atmosphere, chromium nitrides are formed, once chromium has great affinity for nitrogen[4]. Vacuum sintering should produce similar properties to those obtained under H_2 atmosphere[2].

Pre-sintering or removal of additives is one of the most important steps in powder metallurgy materials processing for accomplishing suitable corrosion resistance. Binders or lubricants are organic compounds formed by long carbon chains that volatilize at relatively low temperatures. Incomplete removal of these additives can result in high carbon content in the sintered parts, leading to stainless steel sensitization[5].

The corrosion resistance of stainless steels (SS) is directly related to their passive layer composed mainly of chromium oxide (Cr_2O_3)[6]. Materials produced via powder metallurgy (PM) have economic advantages in many applications comparatively to those fabricated by conventional techniques due to their near-final shape. Nevertheless, sintered stainless steels present lower corrosion resistance comparatively to those obtained by conventional metallurgy. The porosity characteristic of PM materials results in increased area exposed to the corrosive environment[7]. Besides, depending on the pores dimension, aeration differential cells are formed, reducing the tendency to passivation of the steel and, consequently the susceptibility to localized corrosion. The incomplete removal of lubricant during pre-sintering process of PM fabrication results in increased susceptibility of localized corrosion of stainless steels sintered parts.

Materials and Methods

AISI 304 L water atomized powder with 1 wt% wax as lubricant were used in the fabrication of the filters tested in this study. Chemical analysis of the powder was performed by X-ray fluorescence. Carbon and sulfur contents analysis was carried out by combustion in a LECO

analyzer. The granulometric range was -100 ± 325 mesh. Samples were compacted uniaxially with a pressure of 150 MPa. The lubricant used was removed in the pre-sintering step, at 450 °C, in a muffle furnace. Sintering was performed at 1150 °C in a vacuum furnace (10^{-2} torr). The sintered samples were characterized by X-ray diffraction, and carbon and sulfur analysis was accomplished by LECO. Thermogravimetric analysis was performed to evaluate the percentage of lubricant used. Polarization tests were completed in 3.5% NaCl solution. Microstructural characterization was carried out by conventional metallography and evaluated by optical microscopy and scanning electron microscopy (SEM) coupled to dispersive energy analysis (EDS).

Results and Discussion

Table 1 shows the results from RX fluorescence analysis for the powder as received and the nominal composition for AISI 304L steel. It can be seen that the carbon content of the powder used is above the limits specified by AISI standard (0.03 max). Although the powder was specified as AISI 304L, the powder material was provided with the wax, consequently the high carbon content is related to the carbon in the AISI 304 powder. Thermogravimetric analyses of the as received powders are shown in Table 2. The tests were completed within the temperature range of lubricant removal and the results showed that all wax was removed from the starting powder.

Table 3 shows the RX fluorescence analysis of sintered AISI 304 SS. A comparison with Table 1 shows chromium content variation between the powder and the sintered material. For stainless steels sintering at 1300 °C, pressures of 25 to 65 Pa are typical. Chromium vapor pressure at 1205 °C is 13 Pa, explaining the loss of chromium during sintering. Chromium loss of sintered powder A was around 4%, whereas that of sintered powder B was 1.7 %. The vapor pressure of some elements, such as chromium, at certain temperatures is close to the pressure reached in conventional vacuum furnaces with only a mechanical pump system. Consequently, chromium content may be reduced in a typical sintering cycle if the vacuum level is not properly controlled.

Austenitic steels are subjected to sensitization when heated in the temperature range between 400 °C and 900 °C. In this temperature range, chromium and carbon combine to form chromium carbide ($Cr_{23}C_6$) which precipitates preferentially at grain boundaries. In this way, a large amount of chromium is removed from the matrix, increasing the susceptibility to corrosion of the chromium impoverished areas surrounding the grain boundaries

Table 1. RX fluorescence analysis of as received powders.

Element	Powder A (%)	Powder B (%)	Nominal Composition (%)
Cr	18.88	19.68	18.00 a 20.00
Ni	11.28	10.96	8.00 a 12.00
Si	0.85	0.82	1.00 (max)
Mo	0.12	0.21	-
C*	0.055	0.084	0.03 (max)
Fe	Bal.	Bal.	Bal.

Table 2. Weight loss analysis of as received powder.

	Weight variation wt. %
Powder A	1.17
Powder B	1.05

Table 3 shows that the carbon content in the sintered AISI 304 L SS is above 0.03, that is, the sintered SS are not low carbon stainless steels. Removal of the lubricant was done after compaction, in this way carbon residue can be retained in the compacted due to the bond between particles, becoming internal after sintering.

Table 3. RX fluorescence analysis of sintered AISI 304 SS.

Element	Sintered SS with powder A (%)	Sintered SS with powder B (%)	Nominal Composition (%)
Cr	18.05	19.35	18.00 – 20.00
Ni	11.10	10.81	8.00 to 12.00
Si	1.56	0.91	1 (max)
Mo	0.19	0.22	-
C*	0.088	0.077	0.03 (max)
Fe	Bal.	Bal.	Bal.

Figure 1 shows samples A and B after sintering. As can be observed, sintered sample A shows intergranular corrosion attack inside the grains and this is due to steel sensitization. On the other hand, sintered sample B with higher chromium contents than sample A, showed resistance to intergranular attack.

Sintered A   Sintered B
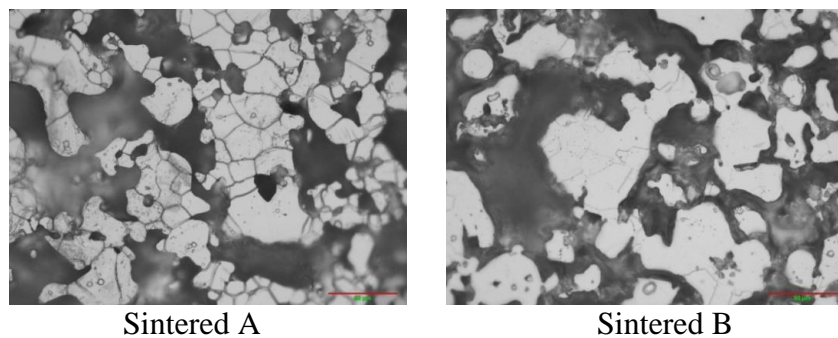
Fig. 1. Micrograph of samples after sintering, obtained by optical microscopy (A) showing sensitized material after sintering and (B) the same effect is not observed in this sample after sintering.

Silicon was found in significant amounts in the sintered samples. According to literature [8], atomized stainless steels normally have an oxygen content of 2000 ppm or more. A large part of this oxide is eliminated during the sintering process; some SiO_2 was retained in grain boundaries, as shown in Figure 2.
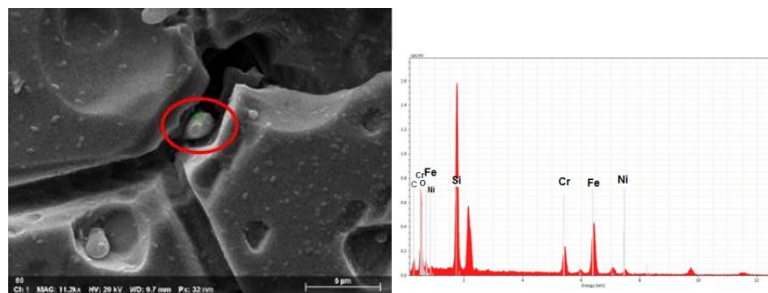

Fig. 2. Sintered sample A showing silicon oxide in grain boundary of the stainless steel.

Figure 3 shows the points on sintered samples A and B where EDS analysis was carried out and Table 4 displays the EDS results. The results show decrease in Cr content at the areas closer to grain boundary for sintered sample A whereas for sample B there was no significant variation in Cr amounts at the analyzed areas. Most importantly, it is the intense grain boundaries (GB) attack in sample A and no attack at GB of sample B. According to literature[9], sensitization is the main cause of selective attack at grain boundaries of stainless steels. Galvanic coupling effects between Cr-impoverished regions and the grain bulk result in a severe corrosion along the grain boundaries. EDS analysis of the grain boundary and attacked area indicated in Fig. 4 for sintered sample A showed high chromium content (26 wt.%), suggesting the presence of chromium precipitate in this zone.
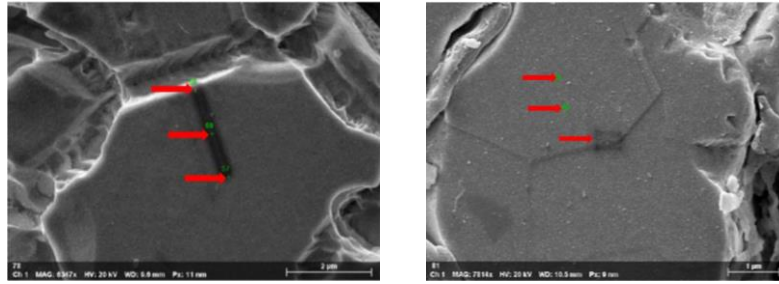
Fig. 3. SEM micrographs showing the points where EDS analysis was carried out in (a) sintered sample A
and (b) sintered sample B.

Table 4. EDS results of analyzes made by on the sintered samples.

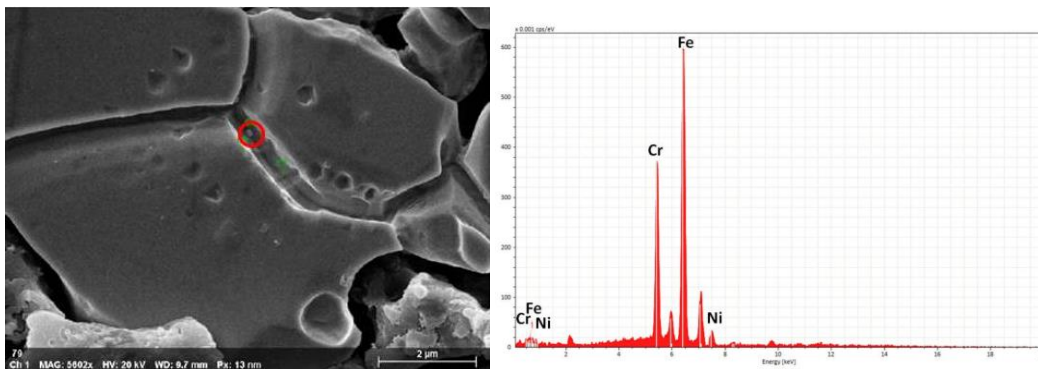| Sintered A				Sintered B		
Point	Fe	**Cr**	Ni	**B**	Fe	**Cr**	Ni
1	70.01	**19.90**	10.10	1	68.87	**20.02**	11.11
2	70.56	**19.50**	9.89	2	69.07	**20.22**	10.71
3	70.11	**19.40**	10.15	3	68.83	**20.20**	10.96

Fig. 4. Sintered sample sintered A showing attacked grain boundaries
and chromium rich precipitate at the corroded zone.

The low corrosion resistance of sintered materials compared to those produced by conventional metallurgy is related to their inherent porosity. In the case of sintered filters, open or interconnected pores might act as crevices where aeration differential cells can develop leading to localized corrosion. Figure 5 presents a schematic illustration of the process involved in initiation of crevice corrosion. Pore shape is very variable and also a difficult parameter to quantify with simple measurements. Porosities also correspond to discontinuities in the passive layer. According to the literature [10], the pore morphology is a parameter more important to corrosion of sintered stainless steels than the porosity itself.
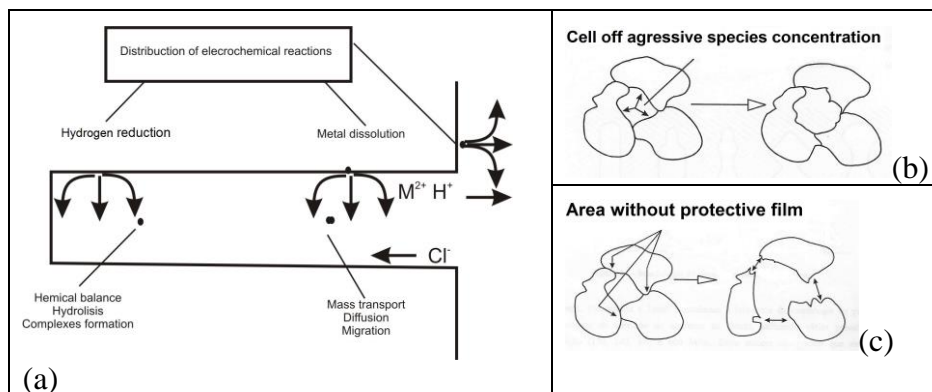

Fig. 5. Crevice corrosion initiation in (a) occluded areas, (b) porosities
and (c) corrosion propagation inside pores.

Polarization curves obtained for the sintered samples A and B are shown in Figure 6. Nobler corrosion potential and a passive region is associated to sintered sample B comparatively to sample A. In this last sample, a pseudo-passive behavior is suggested in the polarization curve with a "breakdown potential" (indicated by arrow) at potentials around -0.1 V (SCE). These results support the previous indication that sensitization occurred in sintered sample A.

According to the literature [11], adsorption of chloride ions might lead to passive film breakdown. The most susceptible areas to depassivation are the Cr-impoverished ones related to sensitized zones. In the case of the present study, besides sensitization the sintered filters have porosities that contribute to a non-homogeneous passive film with discontinuities. Considering that both tested filters presented similar porosity, sensitization was the main cause of higher susceptibility of sample A to intergranular attack and this was due to its higher C and lower Cr contents.
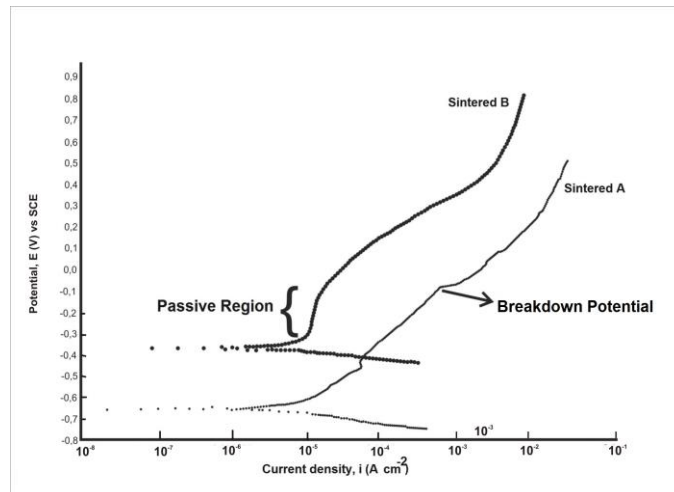

Fig. 6. Polarization curves of sintered samples A and B obtained in naturally aerated
3.5 wt% NaCl solution.

Conclusions

A higher susceptibility to intergranular corrosion was associated to the filter tested that presented higher C and lower Cr contents after sintering (Filter A). Sensitization was associated to this particular filter, whereas the other type of filter (Filter B) showed a high resistance to intergranular corrosion attack.

Acknowledgements

Refernces

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