Effect of heating mode and Y$_2$O$_3$ addition on electrochemical response on austenitic and ferritic stainless steels

A. Raja Annamalai$^1$, A. Upadhyaya$^2$ and D. K. Agrawal$^3$

The present study compares the effect of Y$_2$O$_3$ addition and heating mode on the electrochemical response on austenitic (316L) and ferritic (434L) stainless steel during solid state sintering. Up to 12 vol.-%Y$_2$O$_3$ was added to 316L and 434L stainless steel. The compacts were sintered at 1350°C for 60 min. The sintered samples were characterised for their density and hardness. The effect of heating mode and Y$_2$O$_3$ addition on the microstructural evolution and electrochemical (corrosion) response for the microwave sintered samples are compared with conventionally sintered samples. The density of stainless steel samples sintered through the microwave sintering was higher than that of conventional sintering.

Keywords: Powder metallurgy, Sintering, Hardness, Electrochemical techniques

Introduction

Stainless steels produced by powder metallurgy (PM) are widely used in automotive and structural applications. Powder metallurgical processing offers the advantage of low cost net-shaping with high material utilisation (95%), relatively low temperature processing, and a more refined and homogeneous microstructure. Austenitic stainless steels (316L) have been widely used in a variety of product forms for architectural, biomedical, industrial and nuclear applications owing to its excellent corrosion and oxidation resistance, good strength, excellent toughness and fabrication properties. Ferritic stainless steels possess a good combination of radiation as well as corrosion resistance. The ferritic stainless steels with fine oxide dispersoids are reported to have comparable high temperature properties as those of austenitic stainless steels. Extensive research was carried out on the effect of Y$_2$O$_3$ on the sintering behaviour and corrosion resistance of 316L stainless steel by Lal and Upadhyaya and Shankar et al.$^{5,6}$ Solid state sintering was carried out on 316L austenitic powders and the effect of up to 8 vol.-%Y$_2$O$_3$ addition was examined. It was observed that the sintered porosity was more homogeneous for the Y$_2$O$_3$-containing composites than for the straight 316L under identical sintering conditions. This was attributed to the interaction of Cr$_2$O$_3$ with the Y$_2$O$_3$ dispersoids. Maximum tensile strength was obtained for the sample containing 4 vol.-%Y$_2$O$_3$. The hardness of the samples increased with increasing percentage of Y$_2$O$_3$, Shankar et al.$^{5,6}$ investigated the effect of sintering temperature and yttria addition on electrochemical behaviour of PM ferritic and austenitic stainless steel in acidic and chloride environment through polarisation methods. They showed that the corrosion behaviour of yttria-dispersed stainless steel is comparable that of the corresponding unreinforced stainless steels. The beneficial effect of yttria aluminium garnet (YAG) addition on the densification and hardness of the ferritic and austenitic stainless steel is previously reported by Jain et al.$^8$ Balaji and Upadhyaya$^9$ and Tiwari et al.$^{10}$ have examined in detail the electrochemical response of the YAG added 316L and 434L stainless steels. However, one of the limitations of using higher sintering temperatures is microstructural coarsening. Typically, in conventional (electrically heated) furnace compacts get heated through radiation mode during sintering.$^2,11$ Consequently, to prevent thermal gradient within the compact, a slower heating rate coupled with isothermal holding at intermittent temperatures is provided, which increases the process time, thereby, contributing to coarsening. To eliminate this problem, a faster heating rate during sintering is envisaged. However, faster heating rates in conventional furnaces result in a thermal gradient within the compacts and led to distortion and inhomogeneous microstructure of the sintered compacts. One of the techniques to achieve relatively homogeneous as well as fast sintering in compacts is through microwave heating.$^{12}$ Microwaves directly interact with the individual particulates within the pressed compacts and thereby provide rapid volumetric heating. This reduces processing time and results in energy saving. A range of metallic systems have been shown to couple with microwaves.$^{13,14}$ Among ferrous systems, Anklekar et al.$^{15,16}$ and Raja Annamalai et al.$^{17,18}$ have recently demonstrated that steel powder compacts can be effectively sintered in a microwave furnace and yield higher mechanical properties as

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Comparison of conventional sintering. Saitou,19 Panda et al.20 and Padmavathi et al.21 have demonstrated that both austenitic as well as ferritic stainless steel compacts can be consolidated using microwaves. Padmavathi et al.21 have shown that 316L–YAG composites can be prepared by microwave sintering and have a superior mechanical and corrosion response. While much emphasis has been laid on the mechanical property response of PM stainless steel, little systematic work has reported on their corrosion response. The response of heating rate on YAG added 316L stainless steels have been examined in detail by Panda et al.22,23 However, the electrochemical response was not dealt by them. Chen et al.24 have shown that number of fine spherical yttrium-rich oxide particles are not evenly distributed in the steel matrix at 1100°C in rolling conditions; Yu et al.25 found that up to 0.5% yttrium addition to K38 nano-crystalline coatings have resulted in significant improvement of high temperature oxidation resistance. However, till date as per the author’s knowledge no investigation was observed on microwave sintering of Y2O3 addition on stainless steels. In this work, an attempt has been made to study the effect of heating mode on densification response, mechanical and electrochemical properties of austenitic stainless steel (AISI 316L) and ferritic stainless steel (AISI 434L) using potentiodynamic polarisation techniques.

**Experimental procedure**

For the present investigation, austenitic and ferritic grades were selected. The nominal compositions of the powders used in the present investigation are presented in Table 1. For both grades, the powders were prepared by gas atomisation and were in prealloyed form. The characteristics of the as received powders are detailed in Table 2. For both the grades, yttria powder was mixed in different proportions (4, 8 and 12 vol.-%) in a turbula mixer (model: T2C; supplier: Bachofen, Basel, Switzerland) for 30 min. The powders were then uniaxially pressed to cylindrical pellets (16 mm diameter, and 6 mm height) 600 MPa in a hydraulic press (model: CTM-50; FIE, Ichalkaranji, India). To minimise the friction along the walls of die, zinc stearate was used as a die wall lubricant. Conventional sintering of green compacts was carried out in a MoSi2 heated horizontal tubular sintering furnace (model: OKAY 70T-7; Byssak, Kolkata, India). The compacts were heated at a constant heating rate of 5°C min⁻¹ and isothermally held for 60 min at 1350°C. Two intermediate isothermal holds at 600 and 900°C were provided for delubrication/debinding and reduction of oxides respectively. Sintering was carried out in hydrogen (dew point: −35°C). The microwave sintering experiments were carried out using a 6 kW, 2-45 GHz, multimode microwave furnace. Temperature measurement was made with an optical pyrometer (Raytek, Marathon Series), through a small quartz window at the top of the furnace. The temperature inside the microwave furnace was monitored using an infrared pyrometer by considering the emissivity of steel (0.35). After sintering, the microwave power was switched off and samples were allowed to cool inside the furnace. Further details of the microwave sintering setup used for the present study is provided elsewhere.14,18,20–23 The sintered density was determined using Archimedes method. For microstructural and electrochemical analysis, the samples were polished to mirror finish and ultrasonically cleaned in acetone. The microstructural analyses of the samples were carried out through optical microscope (model: DM2500; Leica Imaging System Ltd, Cambridge, UK). Bulk hardness of the samples was measured using Vickers hardness tester (Leco V-100-C1 Hardness Tester) at 5 kg load. In order to ensure reproducibility, five samples were examined. The scanning electron micrographs of the samples were obtained using back scattered electron imaging mode (Zeiss EVO 50, Carl Zeiss SMT Ltd, UK). The sintered compacts were etched for about 10 s by Marble’s reagent (50 mL HCl + 25 mL of saturated aqueous CuSO4 solution). Before corrosion testing, samples were polished with 600 SiC papers for obtaining a smooth surface and the electrochemical behaviour of the samples was studied in freely aerated 0-1 N H2SO4 solution (pH 1·31 ± 0·4) using electrochemical System (model: VersaSTAT 3; Princeton Applied research). Electrochemical tests were carried out in a flat corrosion cell (Accutrol Inc., USA) using a standard three-electrode configuration with the sample as the working electrode, platinum mesh as the counter electrode and Ag/AgCl (saturated with KCl) as reference electrode (+197 mV w.r.t hydrogen). The exposed area of the sample was 1 cm². Before polarisation, the polished samples were allowed to stabilise for 3600 s in 0-1 N H2SO4 to obtain stable open circuit potential. Electrochemical tests were carried out in a flat corrosion cell (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 w.r.t hydrogen electrode) and the sample as the working electrode. Potentiodynamic polarisation tests were carried out from −250 mV versus open circuit potential to −0.8 V.

<table>
<thead>
<tr>
<th>Composition/wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–16.5Cr–12.9Ni–2.48Mo–0.93Si–0.21Mn–0.025C–0.008S–0.01P</td>
</tr>
</tbody>
</table>

**Table 1 Composition of austenitic and ferritic grade stainless steels used in present study**

<table>
<thead>
<tr>
<th>Grade*</th>
<th>Composition/wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>Fe–16Cr–12.9Ni–2.48Mo–0.93Si–0.21Mn–0.025C–0.008S–0.01P</td>
</tr>
<tr>
<td>434L</td>
<td>Fe–17Cr–1Mo–0.71Si–0.2Mn–0.023C–0.02S–0.02P</td>
</tr>
</tbody>
</table>

*Ametek Specialty Metals Products, USA.

<table>
<thead>
<tr>
<th>Property</th>
<th>Powder Shape</th>
<th>Powder Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing technique</td>
<td>Gas atomisation</td>
<td>Gas atomisation</td>
</tr>
<tr>
<td>Cumulative powder size/m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D10</td>
<td>10.3</td>
<td>8.35</td>
</tr>
<tr>
<td>D50</td>
<td>45.9</td>
<td>35.3</td>
</tr>
<tr>
<td>D90</td>
<td>85.1</td>
<td>75.1</td>
</tr>
<tr>
<td>Apparent density/g cm⁻³</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Flowrate, s/50 g</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>Theoretical density/g cm⁻³</td>
<td>8.06</td>
<td>7.86</td>
</tr>
</tbody>
</table>

**Table 2 Characteristics of powders in as received conditions used in present study**
+1600 mV versus reference electrode at a scan rate of 0.1667 mV s⁻¹. The corrosion potential (E_{corr}) and corrosion rate, passivation current density (I_{pass}), critical current density (I_{crit}), breakdown potential (E_{b}) were determined from the polarisation curves. The corrosion potential (E_{corr}) and corrosion current (I_{corr}) were determined from the intersection of these two linear plots. The corrosion rate (mmpy) can be determined using 1st-Stern method\(^\text{27}\) and is expressed as follows

\[
\text{Corrosion rate} = 0.0033 \frac{E_{corr}}{r I_{corr}}
\]

where, \(e\) is the equivalent weight (g); \(r\) is the density of the material (mg m⁻³), and \(I_{corr}\) the corrosion current (mA m⁻²).

### Results and discussion

#### Densification response

Figure 1a and b shows the effect of heating mode and varying yttria addition (0, 4, 8, 12 vol-%) on the sintered density of austenitic and ferritic stainless steel, respectively. For all the stainless–yttria compositions, microwave sintering results in improved density. Relative to conventional sintering, the effect of densification is more pronounced in 434L–Y₂O₃ composites. From the conventional sintering results, it can be inferred that yttria addition does not adversely affect the sintered density of austenitic stainless steel (Fig. 1a). In contrast, up to 8 vol-% Y₂O₃ addition results in improvement in the sintered density of 434L compacts (Fig. 1b). Another interesting observation from the densification results (Fig. 1) is that for microwave processed 316L–Y₂O₃ as well as 434L–Y₂O₃ composites, the sintered density increases with increasing Y₂O₃ addition. This underscores good coupling between microwaves and yttria. It is also interesting to note that for 434L–Y₂O₃ composites, the compact density attained through microwave sintering increases with increasing yttria fraction (Fig. 1b). The same trend has been observed by few other researchers.\(^\text{20–23}\) In case of conventional sintering, the results from this study (Fig. 1) indicates that up to 8 vol-% Y₂O₃ addition enhances the density of stainless steel compacts. Elsewhere, Jain \textit{et al.}\(^\text{8}\) have also reported the positive influence of YAG addition on the densification enhancement in sintered stainless steel compacts. For
conventionally sintered ferritic stainless steel–yttria composites, the positive role of $Y_2O_3$ addition on the densification can be attributed to the chemical interaction between $Cr_2O_3$ and $Y_2O_3$. Elsewhere, Lal and Upadhyaya have reported that the reaction between the $Y_2O_3$, $Cr_2O_3$ and iron oxide during high temperature sintering to form spinel of type $(YFeCr)_3O_4$ or $(YFe_2Cr)_2O_3$. It is postulated that the formation of

3 Optical micrographs of 316L–$Y_2O_3$ composites with varying amounts of yttria addition (0, 4, 8 and 12 vol.-%) and sintered in conventional and microwave furnace.
these reaction product contribute to the protection of the surface during anodic polarisation.

**Hardness**

Figure 2a and b graphically shows the effect of Y₂O₃ addition and heating mode on the bulk hardness of austenitic and ferritic stainless steel compacts, respectively. As compared to straight stainless steel grades (316L, 434L), the hardness is higher for sintered stainless steel–Y₂O₃ composites. However, among the stainless steel–Y₂O₃ composites, the hardness does not seem to be strongly influenced on the amount of Y₂O₃ addition. For all the compositions, the hardness of microwave sintered compacts is higher than those measured for conventionally sintered compacts.
Microstructural results

The effect of Y$_2$O$_3$ addition and heating mode on the optical as well as SEM microstructures of 316L and 434L stainless steels is presented in Figs. 3–6. All sintered microstructures are characterised by presence of uniform distribution of residual porosity having irregular morphology. Most pores are concentrated at the grain boundaries. For Y$_2$O$_3$ containing composites, the SEM photomicrographs (Figs. 4 and 6) show uniform dispersion of Y$_2$O$_3$ along the stainless steel grain boundaries. For straight 316L and 434L, the microstructure of the microwave sintered compact is more refined (Fig. 3a and 5a). The pores become more rounded and smaller but intragranular when the same steel is processed in microwave sintering. The
comparison of the microstructures of sintered 434L–Y$_2$O$_3$ composites reveals some interesting findings. For conventionally sintered compacts, the grain size reduces progressively with increasing yttria reinforcement. This trend is typical of that observed in sintered particulate metal matrix composites. In case of 316L–Y$_2$O$_3$ composites, the sintering mode does not seem to significantly influence the microstructure (Fig. 3b–d). In contrast, as compared to conventional sintering, the grains appear to be coarser in 434L–Y$_2$O$_3$ composites consolidated through microwave sintering (Fig. 5b–d). Besides, formation of intermediate reaction product, the enhanced densification in the yttria reinforced stainless steel can also be correlated to the grain growth inhibiting effect of the added dispersoids, which induces more grain boundary diffusion. This is manifested prominently in the conventionally sintered 434L–Y$_2$O$_3$ composites (Fig. 3).
Electrochemical study

To investigate the effect of Y₂O₃ addition and heating mode on the corrosion behaviour, electrochemical tests were conducted on the sintered compacts in 0.1 N H₂SO₄. Figure 7a and b presents the potentiodynamic polarisation curves for 316L–Y₂O₃ composites sintered in conventional and microwave sintering furnace, respectively. The corresponding polarisation curves for 434L–Y₂O₃ composites consolidated using both the heating mode are shown in Fig. 8a and b. The zero current potential value for 316L and 316L–Y₂O₃ composites is observed to be around –300 mV, which is in the active passive transition regime – typical for stainless steel²⁹–³¹ – is shown for all sintered compacts. All 316–Y₂O₃ compositions exhibit passivation response during polarisation. Tables 3 and 4 present a summary of the corrosion parameters determined from the polarisation curves. This is reflected in the invariance in the current density with increasing applied voltage up to 1000 mV in the anodic region (Fig. 7a and b). Beyond that, the current density sharply increases with increasing potential.

Table 3 Effect of heating mode and yttria content on passivity parameters of 316L compacts obtained from potentiodynamic polarisation investigation

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering mode</th>
<th>I_corr/mA cm⁻²</th>
<th>E_corr/mV</th>
<th>Corrosion rate/mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>CON</td>
<td>0.65</td>
<td>–404</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>MWS</td>
<td>0.71</td>
<td>–338</td>
<td>43</td>
</tr>
<tr>
<td>316L–4Y₂O₃</td>
<td>CON</td>
<td>1.40</td>
<td>–361</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>MWS</td>
<td>0.86</td>
<td>–339</td>
<td>47</td>
</tr>
<tr>
<td>316L–8Y₂O₃</td>
<td>CON</td>
<td>1.84</td>
<td>–325</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>MWS</td>
<td>0.26</td>
<td>–338</td>
<td>20</td>
</tr>
<tr>
<td>316L–12Y₂O₃</td>
<td>CON</td>
<td>6.01</td>
<td>–339</td>
<td>327</td>
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<tr>
<td></td>
<td>MWS</td>
<td>0.84</td>
<td>–338</td>
<td>43</td>
</tr>
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</table>
Table 4 Effect of heating mode and yttria content on passivity parameters of 434L compacts obtained from potentiodynamic polarisation investigation

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering mode</th>
<th>$I_{corr}$/mA cm$^{-2}$</th>
<th>$E_{corr}$/mV</th>
<th>Corrosion rate/mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>434L CON</td>
<td>86.7</td>
<td>$-462$</td>
<td>4016</td>
<td></td>
</tr>
<tr>
<td>434L CON</td>
<td>10.9</td>
<td>$-341$</td>
<td>591</td>
<td></td>
</tr>
<tr>
<td>434L–4Y$_2$O$_3$</td>
<td>33.4</td>
<td>$-336$</td>
<td>551</td>
<td></td>
</tr>
<tr>
<td>434L–4Y$_2$O$_3$</td>
<td>10.2</td>
<td>$-339$</td>
<td>1969</td>
<td></td>
</tr>
<tr>
<td>434L–8Y$_2$O$_3$</td>
<td>33.4</td>
<td>$-335$</td>
<td>3622</td>
<td></td>
</tr>
<tr>
<td>434L–12Y$_2$O$_3$</td>
<td>10.6</td>
<td>$-342$</td>
<td>2047</td>
<td></td>
</tr>
<tr>
<td>434L–12Y$_2$O$_3$</td>
<td>11.2</td>
<td>$-340$</td>
<td>4173</td>
<td></td>
</tr>
</tbody>
</table>

Microstructures of conventionally sintered (left) and microwave sintered (right) a straight 316L stainless steel and b–d 316L–Y$_2$O$_3$ composites after subjecting it to corrosion in 0.1 N H$_2$SO$_4$.
which reflects a breakdown in the surface passive layer. In contrast to 316–Y$_2$O$_3$, the 434–Y$_2$O$_3$ compacts – particularly, the conventionally sintered ones – exhibit a relatively large critical current density ($i_{\text{critical}}$) in the anodic region. Thereafter it undergoes passivation. The onset of passivation occurs at a rather early stage in case of microwave sintering. The active–passive transition in the 434–Y$_2$O$_3$ composites is reflected as a sudden decrease in the current density during anodic polarization (Fig. 8).

A remarkable observation for both microwave sintered straight 434L as well as 434–Y$_2$O$_3$ composite is that low current density in the passivation region ($i_{\text{passive}}$) is even lower than any of the 316–Y$_2$O$_3$ composition investigated in the present study. The passive current density ($i_{\text{passive}}$) in case for all the microwave sintered 434–Y$_2$O$_3$ compositions was lower than the corresponding corrosion current density ($i_{\text{corr}}$) values (Fig. 8b). From the data presented in Tables 3 and 4, it is evident that the corrosion rates are in general reduced in for microwave sintered compacts. In case of
conventionally sintered 316L stainless steel, Y2O3 addition results in a slight increase in the corrosion rate. In comparison, the corrosion response of microwave sintered 316L remains unaffected by the Y2O3 content. The corrosion rates of 434–Y2O3 compacts are too high to make a relative assessment of the influence of varying yttria addition. However, the high corrosion rates make the comparison between individual compositions rather difficult. In summary, the trend in the corrosion resistance of sintered stainless steel and their composites can be summarised as

**Conventional sintering**

\[
\begin{align*}
316L & \rightarrow 12Y_2O_3 \rightarrow 316L \rightarrow 8Y_2O_3 \rightarrow 316L \rightarrow 4Y_2O_3 \\
\rightarrow & \text{straight 316L} \\
434L & \rightarrow 12Y_2O_3 \rightarrow 434L \rightarrow 8Y_2O_3 \rightarrow 434L \rightarrow 4Y_2O_3 \\
\rightarrow & \text{straight 434L} \\
316L & \rightarrow 4Y_2O_3 \rightarrow \text{straight 316L} \approx 316L \rightarrow 12Y_2O_3 \\
\rightarrow & \text{straight 316L} \rightarrow 8Y_2O_3
\end{align*}
\]

**Microwave sintering**

\[
\begin{align*}
434L & \rightarrow 12Y_2O_3 \rightarrow 434L \rightarrow 8Y_2O_3 \rightarrow 434L \rightarrow 4Y_2O_3 \\
\rightarrow & \text{straight 434L} \\
316L & \rightarrow 4Y_2O_3 \rightarrow \text{straight 316L} \approx 316L \rightarrow 12Y_2O_3 \\
\rightarrow & \text{straight 316L} \rightarrow 8Y_2O_3
\end{align*}
\]

Figures 9 and 10 show the microstructures of the corroded 316L–Y2O3 and 434L–Y2O3 composites respectively. The composites prepared using austenitic grade stainless steel show a uniform, general corrosion whereas in case of ferritic stainless steel show a uniform, general corrosion. In contrast, the corroded surface of the stainless steel compacts results in microstructural degradation at the surface. Similar kind of inadequate densification whereas in case of latter the corroded 316L–Y2O3 and 434L–Y2O3 composites resulted in inadequate densification whereas in case of latter the corroded 316L–Y2O3 and 434L–Y2O3 compacts are too high to make a relative assessment of the influence of varying yttria particles, which lowers the diffusion rate. Microwave sintering of both the stainless steel compacts results in microstructural coarsening and intragranular pores with rounded morphology. Corrosion resistance of microwave processed stainless steels and stainless steel–Y2O3 composites in 0-1 N H2SO4 is higher as compared to that of conventional sintered compacts in case of microwave sintered compacts.

**Acknowledgements**

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**References**