Influence of Aluminium on Dimensional Change of Sintered 430 Ferritic Stainless Steel


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ABSTRACT. Aluminium is added to decrease matrix chromium losses on 430 stainless steel sintered on nitrogen atmosphere. Three different ways were used to add a 3% (in weight) aluminium: as elemental powder, as prealloyed powder, and as intermetallic Fe-AI compound. After die pressing at densities between 6.1-6.5 g/cm$^3$, samples were sintered on vacuum and on N$_2$-5%H$_2$ atmosphere in a dilatometric furnace. Therefore, dimensional change was recorded during sintering. Weight gain was obtained after nitrogen sintering on all materials due to nitrides formation. Sample expansion was obtained on all nitrogen sintered steels with Al additions. Microstructure showed a dispersion of aluminium nitrides when pre-alloyed powders are used. On the contrary, aluminium nitride areas can be found when aluminium is added as elemental powders or as Fe-AI intermetallics. Also nitrogen atmosphere leads to austenite formation and hence, on cooling, dilatometric results showed a dimensional change at austenitic-ferritic phase transformation temperature.

Keywords: Dimensional change, ferritic stainless steels, aluminium additions

1 INTRODUCTION

Ferritic sintered stainless steels are widely used on applications with moderate corrosion resistance and ductility, low temperature or magnetic applications since they are relatively weak at high temperature. The addition of other alloying elements to the nominal composition looks for enhancing certain properties. Improved corrosion resistance by road salt with molybdenum, intergranular corrosion stabilization with niobium, better machinability with sulfur or manganese sulfur, are some examples. On the contrary, elements such us nitrogen, usually introduced during sintering on nitrogen base atmospheres, leads to the formation of chromium nitrides, which may adversely affect stainless steel corrosion resistance. Ceramic or metallic additions could be added to combine with nitrogen during sintering. Nitrides so formed allowed keeping the content of chromium on steel matrix.

On the other hand, aluminium addition is exceptionally effective in enhancing the oxidation resistance of Fe-Cr alloys by the formation of a stable layer of $\alpha$-Al$_2$O$_3$, rather than of Cr$_2$O$_3$ [1]. This has been exploited commercially in a number of materials, such us Fe–20Cr–5Al as substrate materials for catalytic converters that can be used at temperatures of up to 1375°C in the preoxidized condition. An improvement in the oxidation resistance for 316L stainless steel powders is achieved when a combination of grain refinement and alloying with 6 wt.% Al is employed. Mechanical milling (cryomilling and using SPS) is the process of choice for the fabrication of alloyed powders [2].

On the present work, aluminium and intermetallics Al-Fe are added to 430L ferritic stainless steel. Iron aluminide intermetallics are among the promising engineering materials to substitute stainless steel or Ni-based superalloys in high-temperature applications due to their low cost, high specific strength, high melting points, excellent corrosion resistance under oxidizing, carburizing and sulfidizing atmospheres, relatively high electrical resistivity, and low thermal conductivity [3]. The absence of a persistent liquid phase on Fe-Al alloys is overcome when is used Fe-Al intermetallics, meanwhile with elemental powders, a permanent liquid phase is present up to intermetallics formation. This leads to important dimensional changes which would make pressed parts far from the near net shape after sintering. Dimensional changes will be analyzed through a dilatometric study, within a microstructural study of sintered materials.
Vacuum sintering allowed a lower sintering density on 430L stainless steel without additions than N2/H2 sintering atmosphere (Table 1) due to weight gain and a low dimensional change. Low melting point of Al (660°C) leads to a liquid phase on 430L with additions and densification will be carried out on semi-solid state. On the contrary, formation of C3N4 and AIN due to AI2N5 (1169°C) leads to a liquid phase on 430L with additions and FeAI25 (1165°C) and FeN and intermetallics FeAI2 since shrinkage is observed on vacuum meanwhile swelling is obtained on N2-H2 (Table 1). Liquid phase intermetallic Al/Fe powder additions justifies the different swelling on behaviour of intermetallics in vacuum or in N2-H2. Liquid phase nitriding from aluminium or intermetallics melt could reduce the diffusion rate resulting in lower dimensional change. The presence of aluminium leads to highest weight gain on vacuum or in N2-H2. Liquid phase nitriding from aluminium or intermetallics melt could increase the sintered density but swells than on vacuum. Sintered density on vacuum is close to that obtained on N2-H2 atmosphere.

Table 1. Density and dimensional change of green and sintered materials on vacuum and N2-H2 sintering atmospheres.

<table>
<thead>
<tr>
<th>Material</th>
<th>Green density g/cm³</th>
<th>Vacuum Sintering SD%</th>
<th>N2/H2 Sintering SD%</th>
<th>Change in Length %</th>
<th>Weight gain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>430L</td>
<td>6.46-6.50</td>
<td>83.4</td>
<td>83.9</td>
<td>0.05</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe-16Cr-3AI</td>
<td>6.27-6.30</td>
<td>82.7</td>
<td>83.2</td>
<td>1.85</td>
<td>2.98</td>
</tr>
<tr>
<td>430L+3AI</td>
<td>6.33-6.40</td>
<td>78.0</td>
<td>83.4</td>
<td>0.9</td>
<td>1.25</td>
</tr>
<tr>
<td>430L+FeAl2</td>
<td>6.26-6.30</td>
<td>80.7</td>
<td>84.5</td>
<td>0.28</td>
<td>1.10</td>
</tr>
<tr>
<td>430L+FeAl5</td>
<td>6.21-6.26</td>
<td>80.7</td>
<td>82.5</td>
<td>0.44</td>
<td>1.15</td>
</tr>
</tbody>
</table>

3.2 Dimensional change and microstructure of 430L and Fe-16Cr-3AI. Low shrinkage and high swelling are found on prealloyed stainless powders sintering on N2-H2 as a consequence of chromium and aluminum nitriding (point A on curve N2-H2, figures 3 and 4). Also austenite formation is obtained since on cooling, a dimensional change is obtained on the interval of transformation gamma-alpha (Point B on N2-H2 curve, figures 3 and 4). 430L nitridation decreases diffusion mechanisms and leads to a lower shrinkage than on vacuum. Sintered density on vacuum is close to that obtained on N2-H2 due to the weight gain (Table 1).

Figure 3. Dimensional change on dilatometric tests under vacuum and N2-H2 atmosphere and microstructure of vacuum and N2-H2 (right) 430L sintered samples.

At 1000°C densification starts on 430L, but nitridation leads to a further swelling over 1050°C (Point A, curve N2-H2, figure 3). Fe-16Cr-3AI spherical particles retain their identity and internal porosity on sintered material and appear with internal porosity (Figure 4). From sintered steels microstructures, lamellar constituents of CrN are not observed (Figures 3 and 4). The grain boundary nitrides and the mixture of CrN with ferrite are clearly observed (Figure 3) on 430L sintered on N2-H2.

Solid state sintering on N2/H2 of Fe-16Cr-3AI steel is carried out without dimensional change (Figure 4) over 1150°C on heating up to 1050°C on cooling. Densification due to diffusion mechanism and steel nitridation could justify this dimensional behaviour at high temperature. Nitridation starts at temperatures slightly higher than aluminium melting point (Figure 4, Point A), leading to a high swelling. A complete
3.4 Dimensional change and microstructure of 430L with intermetallics. As it can be seen on figures 6 and 7, from 900°C-1000°C on N₂/H₂ atmosphere, linear change is kept constant. Once intermetallic melting point is achieved, linear change did not increase and it slowed down. On the contrary, vacuum atmospheres showed a change on linear change from 1000°C up to sintering temperature. Lower diffusion of Al into Fe leads to a transient liquid with a lower Al content and at higher temperatures than with Al additions.

Once the additive melts, rapid rearrangement of the solid particles occurs during liquid phase sintering when liquid volume is enough. This stage is followed by a rapid densification and chemical potential gradient across the solid and liquid interface. On Fe-Al and Fe-Intermetallic Al/Fe, once aluminium has diffused across the liquid/solid (430L) interface, liquid transient phase disappears and solid state sintering mechanisms govern sintering densification of a clearly inhomogeneous material. When transient liquid solidifies, it is expected a lower Kirkendall porosity at additive particle sites than during liquid phase sintering.

The lower diffusion rate of aluminium from intermetallic powder into the iron compared with elemental Al powder in Fe, coupled with a fast heating rate (150K/min), leads to minimal Fe-Al inter diffusion during heating [6].

Influence of sintering atmosphere can be seen on 430L + Al over 850°C (Figure 5). Thus, aluminium melting point leads to a high swelling (Point B1 figure 5) following by Al diffusion into iron. Intermetallics Fe/Al leads to further swelling up to intermetallics melting (Point A, Figure 5). On N₂/H₂, nitruration of aluminium diffusion areas (dark grey, Figure 5) decreases densification and increases microhardness. A network of chromium nitrides surrounding aluminium diffusion areas can be seen on microstructure.

SEM microscopy suggests [6] that agglomerated intermetallic Fe/Al particles are responsible for a significant portion of the remaining porosity in high sintered density compacts. Intermetallic particles form a liquid during sintering and creating stable pores after melting (Figure 7). Fe₅Al₆ particles retain their identity and they appear as a mixture of FeAl and Fe₅Al₆ phases. At 1000°C reaction Fe + Fe₅Al₆ would lead to complete FeAl formation [7]. On vacuum a high intermetallic particle size allows to find intermetallic phases that should not be present over 1162°C [6]. The formation of intermetallic or aluminium nitration as well as low diffusion mechanisms justifies steel dimensional behaviour on heating over 1150°C up to the end of sintering holding time.
intermediate phases (aluminides of Fe and Cr) at 800°C–1100°C can be expected on the basis of binary and ternary phase diagrams, but they have not been found clearly on studied microstructures.

4. CONCLUSIONS

Nitration of ferritic stainless steels leads to austenite stabilization and its transformation to ferrite during cooling. Nitrides are present as fine particles uniformly distributed on prealloyed Fe-16Cr-3Al stainless steel meanwhile a nitrides network can be seen on 430L stainless steel without additions as well as on 430L stainless steel with Al and Al/Fe intermetallics additions. Dimensional change behaviour of prealloyed powders was shrinkage when sintering is carried out under vacuum and swelling when N₂/H₂ sintering atmosphere is used.

Although N₂/H₂ atmosphere leads to higher density, densification is lower due to nitration. Several transient liquid phases appear during sintering, due to Al or intermetallics melting. Diffusion of liquid into solid and liquid nitration changes the dimensional behavior during sintering of 430L ferritic stainless steel.

REFERENCES