Manufacturing and processing

Sinter-hardening process applicable to stainless steels

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ABSTRACT

Purpose: of this paper was to describe sintered duplex stainless steels manufactured in sinter-hardening process and its usability in field of stainless steels.

Design/methodology/approach: In presented study duplex stainless steels were obtained through powder metallurgy starting from austenitic, ferritic base powders by controlled addition of alloying elements, such as Cr, Ni, Mo and Cu. In the studies apart from the preparation of mixes, Schaeffler’s diagram was taken into consideration. Prepared mixes have been compacted at 800 MPa and sintered in a vacuum furnace with argon backfilling at temperatures from 1200°C to 1285°C for 0.5, 1 and 2 h. After sintering different cooling cycles were applied using nitrogen under pressure from 0.6 MPa to 0.002 MPa in argon atmosphere. Produced duplex stainless steels have been studied by scanning and optical microscopy and EDS chemical analysis of microstructure components.

Findings: Obtained microstructure and mechanical properties of sintered duplex stainless steel strictly depend on the density and the pore morphology present in the microstructure and especially on cooling rate directly from sintering temperature in sinter-hardening process. The lowest cooling rate - applied gas pressure, the mechanical properties and corrosion resistance decrease due to precipitation of sigma phase. Proper bi-physic microstructure was obtained using nitrogen under pressure of 0.6 and 0.2 MPa.

Research limitations/implications: Applied fast cooling rate seems to be a good compromise for mechanical properties and obtained microstructures, nevertheless further tests should be carried out in order to examine its influence on corrosion properties.

Originality/value: The utilization of sinter-hardening process combined with use of elemental powders added to a stainless steel base powder shows its potentialities in terms of good microstructural homogeneity and especially working with cycles possible to introduce in industrial practice.

Keywords: Sintering; Sinter-hardening; Powder metallurgy; Duplex stainless steel

1. Introduction

Application of powder metallurgy as a highly cost effective and high performance and possibility of manufacturing products with dimensional stability and shape reproducibility, created chances to manufacture duplex stainless steels with controlled mechanical properties and corrosion resistance. Stainless steels made by powder metallurgy mainly single-phase stainless steels, austenitic and ferritic with desired mechanical properties – ferritic stainless steels and high corrosion resistance – austenitic one, for many years have stable position on market of sintered components. The powder metallurgy stainless steels, especially ferritic grades, have found applications in mounting brackets for the rear view mirrors, the tone wheels for the antilock brake systems and also in automotive exhaust applications like exhaust flanges and mounting unit of HEGOS. The automotive market introduces newly designed sintered parts in large amounts in
produced cars. Stainless steel is the preferred material for powder metal flanges because of its resistance to corrosion and oxidation. The fact that the powder metal parts can be made in high material densities for the optimum combination of properties has encouraged their use by biggest users of powder metal exhaust system flanges in the world [1-3]. Application of PM technology for stainless steels manufacturing enables to obtain strictly controlled chemical composition, microstructure and phase composition of alloy and furthermore elimination of many technological difficulties encountered when traditional casting technology were used. It must be noted, that when applying traditional sintering method of stainless steels powders in hydrogen atmosphere without controlled cooling after sintering, precipitations of hard and brittle rich in chromium and molybdenum intermetallic sigma phase may occur. Presence of this phase in microstructure is highly negative and influences the mechanic and corrosion properties of stainless steel. In such case to obtain stainless steel with good mechanical properties and corrosion resistance after sintering stage additional heat treatment is necessary [4-8].

Sintered duplex stainless steels can be made using different methods. First of them is based on sintering of atomized alloyed duplex powder that exhibits limited compressibility due to high alloying element concentration. The main advantage of using alloyed duplex powder is possibility of introducing nitrogen in alloy ensuring in this manner higher mechanical properties and corrosion resistance. The second method concerns sintering mixture of ferritic and austenitic powders in adequate proportion that when compared to sintered alloyed powders give better results in terms of mechanical and corrosion properties and constituted bi-phase microstructure. However, real duplex microstructure forms during cooling stage in contact areas between ferritic and austenitic phases trough segregation of alloying elements chromium and nickel due to diffusion. Next method of manufacturing duplex microstructure is sintering of prepared powders mix obtained through controlled addition of alloying elements promoting formation of austenite or ferrite to single-phase powders both ferritic and austenitic. Alloying element may be added in form of single elements or in combined form [4-19].

2. Experimental procedure

To produce sintered duplex stainless steel different compositions have been tested, using austenitic X2CrNiMo17-12-2 (AISI 316L) and ferritic X6Cr13 (AISI 410L) as starting base water atomized powders of Hoganas Corporation (table 1). X2CrNiMo17-12-2 austenitic base powders were mixed with addition of alloying elements powders such as Cr (in form of ferrochromium powder), Ni, Mo and Cu in the right quantity to obtain the chemical composition similar to biphasic one - mixtures A and B. Powder mixtures designed as C and D were produced starting from ferritic powder X6Cr13. Moreover, the ferritic stainless steel X6Cr17 powder has been admixed to austenitic stainless steel powder in the ratio of 1/1 in order to examine the microstructure derived after sintering (mixture E) and fully austenitic powder X2CrNiMo17-12-2 to compare the corrosion resistance (sample F).

### Table 1. Average composition of starting powders

<table>
<thead>
<tr>
<th>Grade powder</th>
<th>Elements concentration, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN-EN10088</td>
<td>AISI Ni Cr Si Mn Mo C Fe</td>
</tr>
<tr>
<td>X2CrNiMo17-12-2</td>
<td>316L 13 17 0.8 0.2 2.2 0.02 bal.</td>
</tr>
<tr>
<td>X6Cr13</td>
<td>410L 0.14 12.2 0.88 0.09 - 0.02 bal.</td>
</tr>
<tr>
<td>X6Cr17</td>
<td>430L - 16 1.14 0.19 - 0.09 bal.</td>
</tr>
</tbody>
</table>

In the preparation of powder mixtures, Schaeffler’s diagram was taken into consideration, thus Cr_{eq} = %Cr + %Mo + 1.5%Si + 0.5%Nb and Ni_{eq} = %Ni + 30%C + 0.5%Mn equivalents were obtained. The weight quantities of the corresponding elements in percent were introduced in those formulas which locate all prepared powder mixtures in a well defined area, at least from a theoretical point of view. Chemical composition of produced mixtures was placed in austenitic-ferritic area of the Schaeffler’s diagram with various content of ferritic phase. Table 2 presents all prepared compositions according to Schaeffler’s diagram and table 3 their calculated chromium and nickel equivalents on diagram.

### Table 2. Chemical composition of investigated powder mixes

<table>
<thead>
<tr>
<th>Base powders</th>
<th>Composition designation</th>
<th>Elements concentration, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN-EN10088</td>
<td>Ni Cr Si Cu Mn Mo Fe</td>
<td></td>
</tr>
<tr>
<td>X2CrNiMo17-12-2</td>
<td>A 10.52 26.40 0.80 0.80 - 2.02 bal.</td>
<td></td>
</tr>
<tr>
<td>X2CrNiMo17-12-2</td>
<td>B 11.51 21.33 0.84 2.00 - 2.21 bal.</td>
<td></td>
</tr>
<tr>
<td>X6Cr13</td>
<td>C 8.10 22.72 0.70 - 0.06 2.00 bal.</td>
<td></td>
</tr>
<tr>
<td>X2CrNiMo17-12-2</td>
<td>D 8.09 26.23 0.65 2.00 0.06 2.00 bal.</td>
<td></td>
</tr>
<tr>
<td>X6Cr17</td>
<td>E 6.50 16.20 1.02 0.05 0.10 1.25 bal.</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3. Chromium Cr_{eq} and nickel Ni_{eq} equivalents of prepared powder compositions

<table>
<thead>
<tr>
<th>Composition designation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr_{eq}</td>
<td>30.33</td>
<td>25.68</td>
<td>26.57</td>
<td>30.01</td>
<td>19.48</td>
</tr>
<tr>
<td>Ni_{eq}</td>
<td>11.25</td>
<td>12.30</td>
<td>8.97</td>
<td>8.86</td>
<td>8.95</td>
</tr>
</tbody>
</table>

Acrawax was used as lubricant in a quantity of 0.65 wt.% for all compositions produced. Samples were obtained using a hydraulic press applying a pressure in the range of 500-800 MPa with a floating die. The dewaxing process was done at 550°C for 60 minutes in a nitrogen atmosphere. Samples were then sintered in a vacuum furnace with argon backfilling at temperatures 1200°C, 1260°C, 1285°C, for 30, 60 and 120 min. After sintering different cooling cycles were applied using nitrogen under pressure 0.6MPa (4.1°C/s), 0.2MPa (2.0°C/s), 0.042MPa (1.5°C/s), 0.002MPa (0.1°C/s) in argon atmosphere and 0.006MPa (0.1°C/s) in nitrogen atmosphere.
Densities were evaluated using the water displacement method. Microstructure observations were carried out using light microscope and scanning electron microscope equipped in EDS. Evaluations of the phase composition were made using X-ray spectrometer. Mechanical properties were evaluated basing on the tensile test performed according to PN-EN 10002-1 standard on samples prepared according to ISO 3928 standard and Charpy impact test were performed. Corrosion properties were studied through salt spray test according to BSI 7479:1991 in 5%NaCl solution and immersion test in 5M H2SO4 solution. The pitting corrosion behaviour also was studied basing on analysis of polarization curves in 1M NaCl at room temperature, corrosion rate was calculated according to Tafel method.

3. Results and discussion

The analysis of density measurements shows that for the ferritic based mixtures higher sintered densities were obtained than for the austenitic X2CrNiMo17-12-2 based powders even though starting with green values similar to the other compositions. Density of compositions C and D is situated in the range 7.13–7.15 g/cm³ where for A and B in the range 6.95–7.01 g/cm³. For composition E obtained by mixing ferritic and austenitic powders in equal amounts density shows good values after sintering cycle, about 7.2 g/cm³. Porosity of manufactured steels (Fig. 1) differ between compositions and is strictly conceded with obtained density and decrease with sintering time and temperature.

This effect may be connected to the higher reactivity of ferritic grade powders when comparing to austenitic grades results in higher shrinkage rate of the first one. Furthermore, addition of element like copper results in liquid phase formation during sintering and through it influences the growth of sinterability caused by faster mass transport. This is evident for compositions containing this alloying element with reason of higher sintered density when compared to sintered duplex stainless steels without copper addition. The shrinkage occurring after sintering is relatively high for industrial application in present stage of research and is highest for ferritic base compositions C and D (Fig. 2) obtained during sintering in 1260°C for 60 min.

Analyzing the influence of technological parameters of sinter-hardening process on density, it can be concluded that prolonged sintering time in 1260°C from 30 to 120 min gives greater increase density than sintering in higher temperature 1285°C for all studied materials. Modification of gas pressure in range from 0.6 MPa (rapid cooling) to 0.002 MPa (slow cooling) under direct cooling from sintering temperature doesn't influence the change of density, but utilization of nitrogen during entire sintering and cooling cycle under low pressure of 0.006 MPa decreases density of all prepared compositions (Fig. 3). For single-phase austenitic powder sintered under the same conditions in 1260°C for 60min as-sintered density equal to 7.2 g/cm³ were achieved.

Mechanical properties and corrosion resistance of sintered stainless steels greatly depend on density and particularly its morphology. Basing on observations performed in unetched conditions the differences in pore morphology between sinters can be seen. Austenitic base powders sinters exhibit less favorable pore morphology, in composition A pores are irregular and connected in contrast to ferritic base powders sinters where pores are small, rounded and uniformly distributed in the microstructure. Analysis of pore shape factors \( f_s = 4A/P^2 \) and \( f_e = D_{min}/D_{max} \), where \( A \) and \( P \) are the area and the perimeter, respectively and \( D_{min} \) and \( D_{max} \) are...
the minimum and the maximum Feret diameter of a pore, shows increase of pore shape regularity caused by prolonged sintering time and simultaneously decreases mean pore size. During sintering in 1260°C changes in sintering time from 30min to 120min result in increase of pore with shape factor \( f_s = 0.7 \) from 30-40% up to 50% (Fig. 4). In these sintering conditions shape factor \( f_e \) distribution increases to value 1 what testifies higher pore roundness and decreases pores irregularity. Sintering in higher temperature (1285°C for 60min) result in more rapidly increase of pore shape parameter \( f_e \) to value 1 (Fig. 5) and results in increase of mean pore size, caused by coagulation of smallest pores and simultaneously their higher roundness.

![Fig. 4. Sintering time influence on the pore shape factors a) \( f_e \) and b) \( f_s \) of steel D sintered in vacuum in 1260°C](image)

![Fig. 5. Sintering temperature influence on the pore shape factors a) \( f_e \) and b) \( f_s \) of steel D sintered in vacuum for 60min](image)

Performed metallographic examinations and x-ray (Fig. 6, 7) analysis show bi-phase microstructure of manufactured sintered stainless steels composed of austenite and ferrite (Fig. 8) with variable amount of both phases dependent on applied cooling rate directly form sintering temperature. Correct bi-phase microstructure without any precipitations of intermetallic phases was obtained during rapid cooling using gas pressures of 0.6MPa and 0.2MPa (Fig. 7). Microstructure of stainless steel based on austenitic powder X2CrNi17-12-2 is a mixture of \( \alpha + \gamma \), in case of steel A in austenitic phase twinned grains can be seen and \( \gamma \) phase is uniformly distributed with ferritic grains (Fig. 9). Microstructure of steel B, in matrix of austenite, relatively large island of ferritic grains are present. This non-homogenous microstructure may be caused by insufficient portion of alloying powder Fe-Cr in base powder mixture which activates sintering process and formation of ferrite. The microstructure of duplex stainless steels C and D based on ferritic X6Cr173 powder is well formed and composed of mixture \( \alpha \) + \( \gamma \) where individual grains are fine and well mixed (Fig. 10). In both cases, the formation of lenticular austenite was revealed. Performed analyses do not demonstrate other secondary phases like sigma phase, carbides or nitrides precipitations in the microstructure of steels sintered in this conditions. To compare obtained microstructure after sintering, mix of austenitic X2CrNiMo17-12-2 and ferritic X6Cr17 powders in equal amounts were sintered (Fig. 11). Manufactured steel exhibits a coarse grained microstructure with characteristic subgrains of duplex composition identified as an interdiffusion zone - a sharp and thin microstructure [7]. This intermediate phase, posses chemical composition and microhardness values between those characteristic for surrounding austenite and ferrite. Main conclusion deriving form microstructures of manufactured duplex stainless steels is the possibility of application sinter-hardening process with rapid cooling as well as powder mixtures preparation to ensure desired balance between phase concentration and elements partitioning between phases. The addition of alloying element powders (promoting formation of ferritic and austenitic phase) to master alloy powder, makes possible the formation of microstructures and therefore properties of sintered duplex stainless steels. Utilization of sinter-hardening process to fully single-phase stainless steels ensures required microstructure of final alloy (Fig. 12) as well as properties in terms of mechanical properties and corrosion resistance.

![Fig. 6. X-ray diffraction patterns of manufactured sintered steels sintered in vacuum in 1260°C for 60min and rapid cooled using nitrogen under pressure of 0.6MPa](image)

![Fig. 7. X-ray diffraction patterns of composition A sintered in vacuum in 1260°C for 60 min and cooled using nitrogen under pressure of a) 0.6MPa, b) 0.2MPa, c) 0.042MPa, d) 0.006MPa, e) 0.002MPa](image)
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Fig. 8. Microstructure of composition C, sintered in 1260°C for 60min and rapidly cooled by nitrogen under pressure of 0.6MPa

Fig. 9. Microstructure of composition A, sintered in 1260°C for 60min and rapidly cooled by nitrogen under pressure of 0.6MPa

Fig. 10. Microstructure of composition D, sintered in 1260°C for 60min and rapidly cooled by nitrogen under pressure of 0.2MPa

Fig. 11. Microstructure composition E, sintered in 1260°C for 60min and rapidly cooled by nitrogen under pressure of 0.6MPa

Fig. 12. Microstructure of X2CrNiMo17-12-2 steel sintered in 1260°C for 60min and rapidly cooled by nitrogen under pressure of 0.6MPa

Analyzing the chemical composition of manufactured sintered duplex stainless steels EDS analysis were performed on individual structural components. Basing on it results the concentration of ferrite former elements like Cr and Mo in ferrite region is higher while concentration of Ni is lower than in austenitic region. Element partitioning between both phases is consistent with the stabilizing effect of each element on the respective phase.

Analyzing influence of sintering parameters on the phase composition of analysed duplex steels the prolonged sintering time (in 1260°C from 30 to 120min) influences the increase of austenite content in microstructure while sintering in higher temperature (1285°C for 60min) increases the ferritic phase content. For composition designed as C, the approximate balance of ferrite and austenite was archived (table 4), for this composition Cr_{Ef}=26.57 and Ni_{Ef}=8.97. Portion between phases in microstructures is in accordance with the direction of phase transformations in duplex steels (α + γ → α + γ) and with decrease of gas pressure during cooling stage that is with slower
cooling, the quantity of austenite increases and from ferritic phase intermetallic sigma α-FeCr phase precipitates (Fig. 13). The presence of sigma phase was revealed during slow cooling using gas pressure of 0.006 and 0.002 MPa and with increase of its amount mechanical properties and corrosion resistance decreased, even when cooling with 0.042MPa.

Table 4.

<table>
<thead>
<tr>
<th>Phase quantity, %</th>
<th>Composition designation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Ferrite</td>
<td>75</td>
</tr>
<tr>
<td>Austenite</td>
<td>25</td>
</tr>
</tbody>
</table>

Fig. 13. Microstructure composition A, sintered in 1260°C for 60min and slowly cooled by nitrogen under pressure of 0.002MPa.

Sintered duplex steels rapid cooled after sintering cycle using nitrogen under pressure achieves satisfaction mechanical properties in term of tensile and yield strength (Fig. 14). Compositions A and C shows tensile strength about $R_m=550$MPa with elongation of 5-6% for sintering with rapid cooling cycle while composition B shows $R_m=450$MPa with higher elongation up to 8%. Obtained mechanical properties strictly depend on quantity rate of austenite and ferrite in the microstructure of analyzed steels. The highest tensile strength $R_m=650$MPa has been achieved for steel obtained by mixing both austenitic and ferritic powders in equal amounts. Increase of mechanical properties of sintered duplex stainless steels with increasing ferrite content may be explained due to solid solution hardening of Ni and Mo in the ferrite phase. The internal strain hardening between ferrite and austenite due to different coefficients of thermal expansion, and the new growing inter-diffusion zone at particles boundary cause increase of tensile strength and hardness (Fig. 15). Influence of applied backfilling gas pressure during cooling stage is clearly connected with precipitation of hard and brittle intermetallic sigma phase causing microstructure more sensitive to brittle fracture (Fig. 17). Steels slowly cooled after sintering cycle show mixed fracture where cleavage fracture is caused by sigma phase precipitation thus impact energy in these conditions drops to values lower than 30 J.
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Fig. 16. Fracture surface of composition C sintered in vacuum in 1260°C for 30, 60 and 120 min and rapid cooled using nitrogen under pressure of 0.6MPa respectively a), b) and c)

Fig. 17. Fracture surface of composition B sintered in vacuum in 1260°C for 60 min and slowly cooled using nitrogen under pressure of 0.002MPa

Corrosion resistance of analyzed sintered duplex stainless steels, depends on protective gas pressure during cooling from the sintering temperature. Utilization of high gas pressure during cooling stage result in rapid cooling as fast as 0.6 and 0.2 nitrogen gas pressure is applied. Steels obtained with applying the nitrogen cooling with the pressure of 0.6 MPa are characterized with higher resistance to corrosive environment of NaCl and H₂SO₄ than sintered stainless steels obtained through mixing in equal amounts of X2CrNiMo17-12-2 austenitic steel powder and X6Cr17 ferritic steel powder (Fig. 18, 19, 20) when rapid cooled from sintering temperature.

Fig. 18. Relative mass lose during corrosion test in 5M solution of H₂SO₄ of steels sintered in 1260°C for 60min and rapid cooled with nitrogen under pressure of 0.6MPa

Sintered duplex stainless steels manufactured on the base of X6Cr13 ferritic steel powder are characterized with higher resistance to corrosive environment of NaCl and H₂SO₄ than sintered stainless steels obtained through mixing in equal amounts of X2CrNiMo17-12-2 austenitic steel powder and X6Cr17 ferritic steel powder (Fig. 18, 19, 20) when rapid cooled from sintering temperature.

Fig. 19. Salt spray test corrosion rate of steels sintered in vacuum in 1260°C and rapid cooled using nitrogen under pressure of 0.6MPa

Fig. 20. Results of calculated corrosion rate after electrochemical corrosion test of steels sintered in 1260°C for 60min for various sintering cycles
4. Conclusions

Technological conditions of sintering influence the density of newly elaborated sintered ferritic-austenitic steels. It was shown that use of X6Cr13 ferritic steel powders for manufacturing the double phase steels gives higher density after sintering equal 7.13±7.24 g/cm³, and better pore morphology than X2CrNiMo17-12-2 austenitic steel powders for which the density values are included in the range 6.94±7.08 g/cm³. Mechanical properties and wear resistance of individual sintered ferritic-austenitic steels strictly depend on the quantities of individual phase components in the microstructure. The increase of ferritic phase quantity in microstructure influences the increase of tensile strength, yield strength and wear resistance. Increase of austenitic phase content in microstructure of sintered duplex stainless steels is accompanied by ductility and impact energy increase. Among analysed sintered duplex steels the best mechanical properties reach composition obtained by mixing in equal amounts austenitic X2CrNiMo17-12-2 and ferritic X6Cr17 powders which tensile strength is 672±10 MPa and hardness 58,9±0,5 HRA. Whereas the impact energy about 150,4±6,8 J was obtained for composition C manufactured by addition of alloying powders to X6Cr13 base powder. The increase of sigma phase quantity is accompanied by decrease of elongation and impact energy and also corrosion resistance of steels sintered and slowly cooled directly form sintering temperature.

According to achieved results, it was affirmed that utilization of sinter-hardening process with sufficient rapid cooling combined with presented powder mixes preparation allows for manufacturing the sintered duplex stainless steels with required microstructure and thus with good mechanical properties and corrosion resistance ready to be introduced in industrial practice.

Acknowledgements

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References