

SINTERING OF DUPLEX STAINLESS STEELS AND THEIR PROPERTIES

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Abstract

The production of casting duplex stainless steels have been well known since the '50s, but PM duplex are developing just these years; mostly they are studied in universities and research centres and only few quantities are commercialised. Different studies starting from different kind of powders are trying to develop what wrought biphasic alloys represent in the field of casting products: higher mechanical properties and corrosion resistance than austenitic grades, especially a superior resistance in SCC conditions. This study, starting from conventional atomised AISI 410L with an addition of elemental powders, is investigating the possibility of obtaining an austeno-ferritic structure, with all the advantages concerning this kind of material. Different mixes were produced, bi-axially pressed and sintered under a hydrogen atmosphere. Specimens underwent a thermal treatment in order to obtain a precipitate - free structure. Samples were then characterised under different aspects: mechanical, microstructural and corrosion resistance.

Keywords: *sintered duplex steels, corrosion resistance, mechanical properties*

INTRODUCTION

PM stainless steels are subject to continuous development in order to improve their properties and cost effectiveness. Although powder metallurgy technology is assuming a fast growing importance in the realisation of structural parts, very often the use of PM components is limited by their lower properties if compared to wrought parts. In fact, the presence of porosity reduces mechanical properties but, most of all, corrosion resistance. An attempt towards the improvement of properties, in particular corrosion ones, is to be found in all the studies dealing with the production of sintered duplex steels. Different approaches were used to obtain the final desired structures: the production of powders forms a properly chosen master alloy through nitrogen atomisation [1], the combined use of austenitic and ferritic powders in different ratios [2] and the mixing of elemental powders to an either ferritic or martensitic powder [3]. The encouraging results obtained in the research lead to the development of such preliminary studies; as a matter of fact, in order to further reduce porosity, sintering aids, for example boron, have been added to the starting mixtures [4]. Good results were obtained in studies on AISI 316L [5,6] and on liquid phase sintering on boron added Fe-Mo alloys [7].

Duplex powders are currently studied at different universities [11,12] as well as in the major companies producing powders but no standards valid in all markets present are yet to describe the characteristics. Table 1 summarises the most known and published types of duplex powders.

Tab.1. Composition and characteristics of powder mixes derived from literature.

| UNS | Commercial Name | Producer | Comment |
|---------|-----------------|-------------------------------|---|
| S 31803 | 2205 | Anval | Austeno-ferritic duplex steel containing 0.15% nitrogen High mechanical properties and corrosion resistance Powder developed for plasma spray → Big size spheric powder |
| S 32900 | 329 | Anval | Duplex |
| S 32760 | 100 | Anval | Superduplex (25.5 Cr, 6.8 Ni, 3.5 Mo, 0.7 Cu, 0.7 W, 0.25 N)) |
| | Cold DX Cup | Coldstream | Austeno-ferritic duplex steel with Cu and P to increase compacting properties and final sintered density |
| | 316L+434L | University Carlos III, Madrid | Mix of austeno-ferritic prealloyed powders |
| | 316L+434L | University of Trento | Mix of austeno-ferritic prealloyed powders |

Sintering cycles and atmospheres are not yet properly defined for all these mixes and for this reason most of experiments are oriented towards maximum performance through the optimisation of processing parameters

The present work had its starting point from results obtained in [3,10]. The effects of adding different quantities of boron for further improving of density in sintering were herewith also investigated.

EXPERIMENTAL PROCEDURE

In order to obtain a good mechanical resistance the starting powder chosen was the martensitic 410L exhibiting better properties than 316L, especially if sintering at temperatures higher than 1200°C. The analysis of the average composition of wrought duplex stainless steels and of the Schaffler's diagram determined the base for the preparation of powder mixes which, according to a precedent study [3], should create a double-phase microstructure.

The starting point was that of using a fully martensitic powder (410L) to which single elements were added in order to obtain the calculated theoretical composition.

An extension of the study lead to the addition to the aforementioned mixes of different quantities of elemental boron for each composition. The effects of adding 0.2 and 0.4% mass boron to the microstructure and to the other properties was evaluated.

Compositions D1 and D3 were calculated and realised with the aim of keeping the Ni equivalent values high while diminishing the quantities of elemental Ni and increasing Mn. This was done in order to reduce costs and to decrease the potential mixture biochemical hazard. Composition D4 is characterised by the same Cr eq. and Ni eq. values of D3, but without Mn; in this case the goal is to be able to create comparable mixtures and final products. Unfortunately the approach chosen for the production of duplex components mixing elemental powders gave no chance of diffusing nitrogen in the composition without getting the nitride formation. For this reason, in order to keep PRE levels high, all the other

element quantities were increased, with the aim of staying in the austeno-ferritic area of Schaffler's diagram.

Tab.2. Composition and characteristics of tested powder mixes. Mn added was in the electrolytic form.

| Powder code | Elements [%] | | | | | | | Cr eq. [%] | Ni eq. [%] | (*)PRE w [%] |
|-------------|--------------|------|------|------|------|------|---------|------------|------------|--------------|
| | Ni | Cr | Si | Cu | Mn | Mo | Fe | | | |
| 410-4 | 5 | 20.3 | 0.7 | | 1.5 | 2.5 | balance | 23.85 | 5.84 | 28.55 |
| 410-6 | 8 | 26.4 | 0.6 | 2 | 0.06 | 3 | balance | 30.3 | 8.09 | 36.3 |
| D 1 | 7.5 | 21.1 | 0.4 | 0.19 | 2 | 2 | balance | 23.7 | 8.62 | 27.7 |
| D 3 | 10 | 24.5 | 0.44 | 0.2 | 4 | 3.65 | balance | 28.81 | 12.27 | 36.545 |
| D 4 | 12 | 24.5 | 0.44 | 0.2 | 0 | 3.65 | balance | 28.81 | 12.27 | 36.545 |

(*) PREw stays for Pitting Resistance Equivalent number (PREw = % Cr + 3.3 x (% Mo+0.5% W) + 16x% N)

Powders were mixed using a laboratory double body V 5 litre mixer, having a counter - rotating shaft. Acrawax was used as lubricant in a quantity of 0.75 wt.% in excess 100 for all compositions produced. Samples were obtained using a bi-axial 1000 kN hydraulic press, in a TRS mould (10x10x55 mm). Different compacting pressures were used, i.e.: 500, 600 and 700 MPa. Moreover a specific study aimed at evaluating powder compressibility was carried out.

The debinding was done at 550°C for 30 minutes in a nitrogen atmosphere. Samples were then sintered in a horizontal tube furnace in a protective hydrogen atmosphere at 1240°C for 1 h. Average heating rate was 15°C/min. Densities were evaluated using the water displacement method. For a correct microstructure observation, after polishing samples were etched with different reagents. Microstructure observations were carried out using an optical microscope and a SEM, the latter being used, together with EDS microprobe, for phases distribution and mapping. Hardness values were evaluated using HV10, as recommended for untreated sintered materials [8]. Sintered samples showed precipitate rich microstructures, with predominant ferrite and some austenitic and martensitic areas. Such types of microstructure determine a brittle mechanical behaviour; in order to optimise the structure an annealing treatment was carried out at 1070°C for 30 min followed by a rapid cooling under flowing hydrogen. Cooling speed was measured with a thermocouple and found to be in the range of 600 to 700°C/min. This proves to be fast enough to obtain fully duplex structures, at least according to CCT curves for wrought steels [9].

Corrosion tests were evaluated suspending samples in a H₂SO₄ solution 0.5M at room temperature. Results are herewith reported in terms of grams lost per dm². Measurements were done every 24 hours. Transverse rupture strength as characteristic mechanical property was determined.

RESULTS AND DISCUSSION

As far as compacting is concerned, in all cases produced mixes without boron did not present lower compressibility than simple 410L. The addition of boron, instead, determined a decrease in compressibility growing with higher B percentages. The following plot report an example of trends obtained.

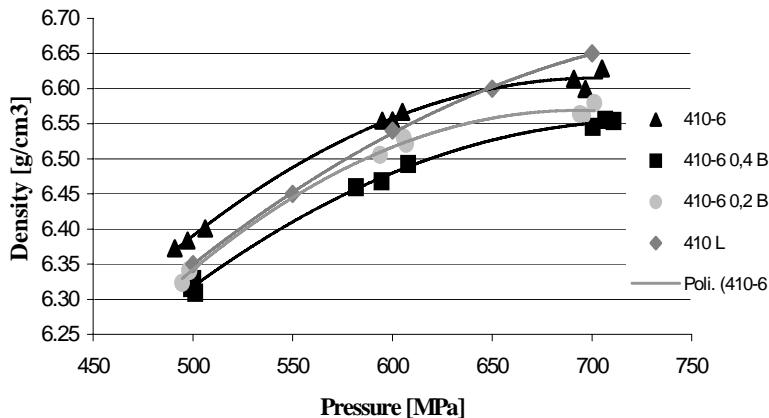


Fig.1. Compressibility curves for starting 410L and different quantities of B added - 410-6 powder mixture

The decrease in compressibility due to the presence of boron is counterbalanced by the fact that, for certain compositions, it is able to form a liquid phase which activates sintering favouring densification. In this case the increase in densification obtained is not proportional to added boron quantities. In almost all cases studied the shrinkage obtained was higher for boron added quantities of 0.2%; however the higher shrinkage did not totally compensate the lower compressibility derived from the addition of B. The following plot shows the relative density of sintered components related to the composition produced.

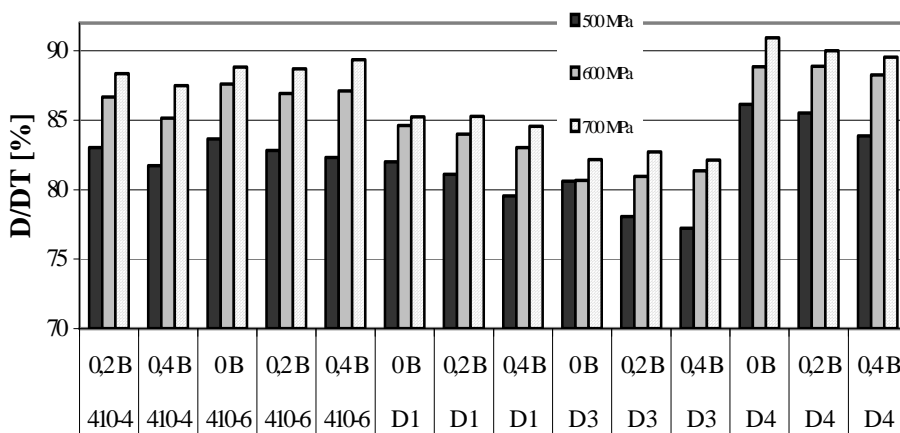


Fig.2. Relative density (D/DT) as function of compacting pressure and powder studied

The formation of a liquid phase during sintering, mainly due to the Fe-B system, even though not determining a full densification, had the effect of closing porosity, increasing the corrosion resistance properties as shown later on.

Compositions rich in Mn did not reach high density values, as already obtained in [3], probably because the high temperature sintering leads to the sublimation of high quantities of manganese rather than to the diffusion of it into the matrix grains. For this

reason composition D1 and D3 were not investigated in corrosion resistance. In any case, future studies will take into consideration the use of prealloyed Mn powders which should minimize sublimation and the possibility of sinter - pressing.

However, densities obtained were relatively satisfying considering that the sintered density of a 316L structure is around 7.00 g/cm^3 (89% of relative density).

Different microstructures could be observed, according to the different composition produced; in the following Figs.3 and 4 some examples are reported.

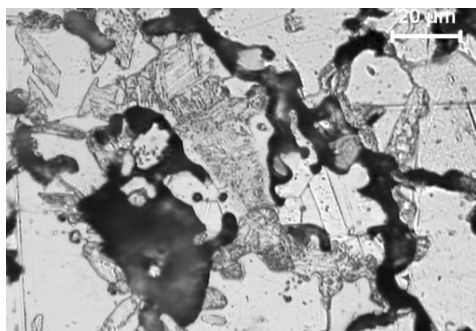


Fig.3. Microstructure of sample 410-6 0B.

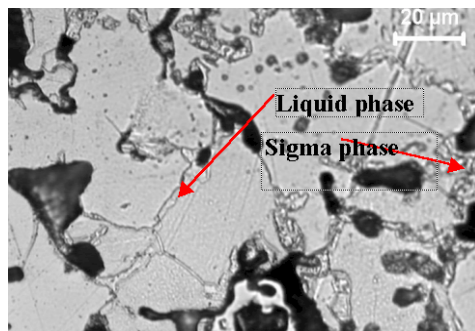


Fig.4. Microstructure of sample 410-4 0.2B.

σ phase precipitates during cooling, as can be seen in the previous figures; Figure 3 shows the presence of σ phase both at the ferrite-austenite grain boundaries and inside ferrite. In this latter case it is reasonable to think that σ phase is finely dispersed together with austenite and deriving from the transformation $\alpha \rightarrow \sigma + \gamma_2$. The eutectoid can form because γ_2 absorbs Ni and rejects Cr and Mo. This contributes to the formation of chromium and molybdenum rich precipitates as the σ phase, depleting the surrounding area of Cr and consequently rendering the structure more susceptible to pitting corrosion.

Figure 4 shows instead a typical microstructure obtained by using mix 410-4 0.2% B. It can be easily noted how the liquid phase penetrates ferritic grains favouring both diffusion and re-arrangement. Also in this case σ phase precipitates are present to a big extent in the matrix.

According to the mechanism that leads to the precipitation of secondary phases, together with the formation of ternary ferro-austeno-martensitic phases that may arise according to Schaffler's diagram, composition D4, having a higher Ni quantity than previous ones, is characterised by a more "complex" microstructure.

Following Figs.5 and 6 show the metallography of treated samples. It can be noted that the microstructure is finer than in previous cases and that no precipitates are visible. Austenite and ferrite are strictly compenetrated.

In Figure 5 it is possible to note that the two phases alternate each other creating different areas both separate and compenetrating; Figure 6 illustrates the alternance of the two phases: a correct balancing is present throughout the structure. In accordance with the optical analysis, and taking into account the starting powder alloy, the three treated material compositions were approximately characterised by the following distribution of phases composition, as shown in Tab.3.

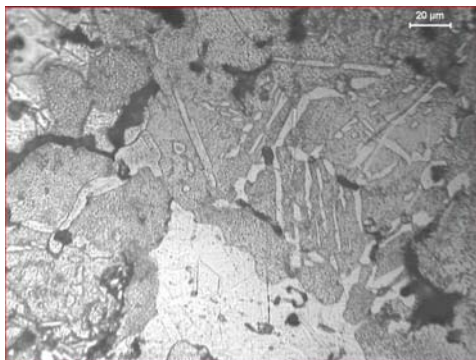


Fig.5. Composition D4 0.2B after TT.

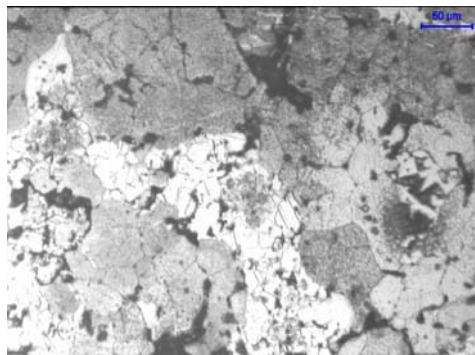


Fig.6. Composition 410-6 0B after TT.

Tab.3. Distribution of ferrite and austenite in the examined structure phases.

| Material | Ferrite | Austenite |
|----------|---------|-----------|
| 410-4 | 60% | 40% |
| 410-6 | 45% | 55% |
| D 4 | 40% | 60% |

Transverse rupture strength values for both untreated and treated samples are shown in Fig.7.

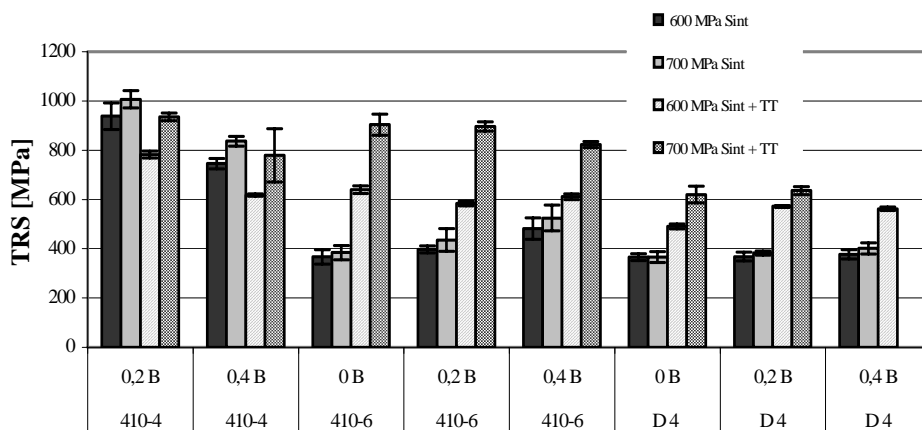


Fig.7. Transverse rupture strength for untreated and treated samples.

The previous plot shows the positive effect of thermal treatment on properties of sintered samples, enhancing the differences between samples pressed at 600 and 700 MPa. Only the low alloyed 410-4 obtained quite good results without thermal treatment; small quantities of alloying elements induced lower precipitation of secondary phases. Probably cooling during sintering was, in this case, rapid enough to prevent the formation of phases lowering the mechanical resistance, as can be noted on CCT curves for low alloyed duplex steels.

Hardness values were included into the range of 140 to 225 HV10. The lower values were obtained for the higher B percentages in all the examined compositions.

The following graphic shows the corrosion rate of suspended samples; the best performance was given by the three 410-6 samples. An important result was given by the addition of B, which considerably decreased the corrosion rate. In particular the 0.2% B materials appeared to be, in all cases, the ones showing better corrosion resistance

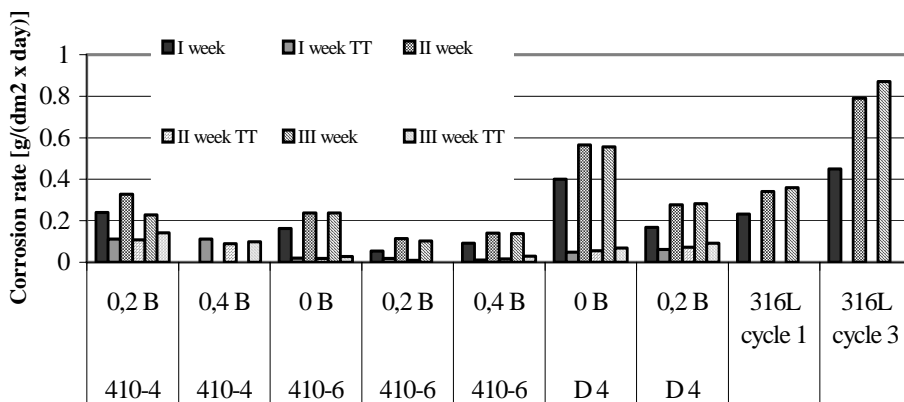


Fig.8. Corrosion resistance in 0.5 M sulphuric acid solution at room temperature of different mix composition evaluated in a three-week period.

The typical corrosion resistance of a 316L grade steel sintered under different conditions (vacuum and a hydrogen based atmosphere at high temperatures) is in the range of 0.2 - 0.7 g/(dm² per day). As it can be noted from the previous figure, results obtained with tested duplex compositions are better: just sintered structures exhibited low corrosion rates but the presence of precipitates has for certain influenced the corrosion making the material sensitive to it, especially in localised areas. Treated samples showed higher corrosion resistance: the solubilisation of precipitates and the following quenching allowed to obtain the real, balanced austeno-ferritic structure.

Generally the co-existence of a ferritic grain close to an austenitic one creates an anodic behaviour in the more active one, thus giving raise to the corrosion phenomena.

For duplex structures, alloying elements make the two phases more stable and, for a general 25% Cr steel, they approximately distribute themselves as in the following Tab.4.

Tab.4. Distribution of different alloying elements in grains for a defined duplex structure.

| | Ferrite | Austenite |
|----|--------------|--------------|
| Mo | 3.8 ± 0.7 % | 2.2 ± 0.3 % |
| Cr | 25.6 ± 0.9 % | 22.3 ± 0.5 % |
| Ni | 4.5 ± 0.3 % | 7.2 ± 0.2 % |

In the ferritic grain the quantity of Cr and Mo is far bigger than in austenite and therefore the pitting index in this case is higher than for austenite. The tendency to passivation is therefore bigger for ferrite that better resists the corrosive attack, creating a

sort of similar resistance to corrosion between the two phases, with a result of hindering the beginning of corrosion.

The presence of a liquid phase, derived from added boron, had positively influenced the corrosion resistance, closing porosity and limiting the penetration of corrosive media into the matrix. The higher the quantity of added boron, the better the resistance even if the difference between the cases with added 0.2 and 0.4 B was negligible.

CONCLUSIONS

The study on sintering of elemental powders starting from 410L allowed to determine the possibility of obtaining a bi-phasic structure made of austenite and ferrite typical of duplex inox steels. Throughout a properly designed thermal treatment a correct balancing between α and γ phases could be obtained. The use of non prealloyed elemental powders showed its potentiality at least in terms of higher compressibility combined with a fair homogeneity, even if working with sintering times and temperatures typical of industrial production.

Obtained densities ($6.9 - 7.1 \text{ g/cm}^3$) were satisfying even though it was thought that boron could have determined a higher densification. Boron has a higher effect on fully prealloyed powders and especially on austenitic based ones. Boron, mixed with elemental powders, did not seem to be able to diffuse into the iron lattice and to form easily the eutectoid as happens when it is added to prealloyed powders. The research is still in progress and it will be focused in future towards the further reduction of porosity.

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