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The PM route for duplex stainless steels

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Although Powder Metallurgy has assumed an important role in the field of massive mechanical industry, a further extension of the market seems to be currently limited by the mechanical properties and corrosion resistance lower than those of wrought parts. This is due mainly by the presence of porosity in the structure which considerably reduces density and contributes to diminish all the other properties. A direction towards which focusing attention is the production of duplex stainless steels; in facts the presence of two different phases in the structure (in different ratios) improves both the chemical resistance and mechanical properties and enhances the thermal characteristics.

In this work it is examined the possibilty of obtaining duplex stainless steels through PM technology starting from martensitic and austenitic powders by simple addition of alloying elements, such as chromium, nichel, molibdenum, manganese, etc.

1. INTRODUCTION

The production of PM duplex is developing just these years. Reaserches 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, so to be able to extend their use to “critical” applications.

Different approaches have been used to obtain the final desired structures: the production of powders from 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].

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 [4]. Duplex powders are studied at different universities [5,6] as well as in the major companies producing powders.

In this work it is examined the possibilty of obtaining duplex stainless steels through PM technology starting from martensitic and austenitic powders by simple addition of alloying elements, such as chromium, nichel, molibdenum, manganese, etc.

The present work had its origin from results obtained in [3,7,8]. Since the main problem related to the traditional sintering in hydrogen without cooling controlling of high alloyed powders, as duplex are, is the formation of secondary phases (mainly sigma), a secondary thermal treatment seems to be needed after sintering [9,10] to obtain a precipitate free structure.

The approach used for this study is however to investigate the vacuum sintering, with a modification of the cycle using nitrogen studied in [3] with argon in order to obtain a precipitate free structure within a single sintering cycle.

2. EXPERIMENTAL

Different compositions have been tested, using 410L and 316L as starting base powders with the characteristics presented in the following table 1.

Table 1:
Average composition of starting powders

[%]	Ni	Cr	Si	Mn	Mo	C	Fe	Cr Eq.	Ni Eq.	PREw*
316 L	13	17	0.8	0.2	2.2	0.02	Bal.	20.4	13.7	24.26
410 L	0.14	12.21	0.88	0.09		0.02	Bal.	13.53	0.305	12.21

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

The following table reports all the prepared compositions.

Table 2:
Composition and characteristics of tested powder mixes.

	Ni	Cr	Si	Cu	Mn	Mo	Fe	Cr Eq.	Ni Eq.	PRE w
316-1	10,52	26,40	0,80	0,80	0,00	2,02	Bal.	30,44	11,25	33,08
316-2	11,51	21,33	0,84	2,00	0,00	2,21	Bal.	25,68	12,30	28,63
410-1	8,10	22,72	0,70	0,00	0,06	2,00	Bal.	26,57	8,97	29,32
410-2	8,09	26,23	0,65	2,00	0,06	2,00	Bal.	30,01	8,86	32,83

Powders were mixed with single elements 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 2000 kN hydraulic press, in a rectangular mould (10x10x55 mm) and in a disc shaped one (40 mm diameter), applying a pressure of 700 MPa. The debinding was done at 550°C for 30 minutes in a nitrogen atmosphere. Samples were then sintered in a vacuum furnace with argon backfilling at 1240°C for 1 h. Rapid cooling was applied, with an average cooling rate of 650 °C/min. This kind of cooling seems to be rapid enough to obtain a fully duplex structure, at least if taking into account the CCT curves derived for the equivalent traditional wrought steels [11].

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.

3. RESULTS AND DISCUSSION

The following graph shows the results obtained in terms of green and sintered density.

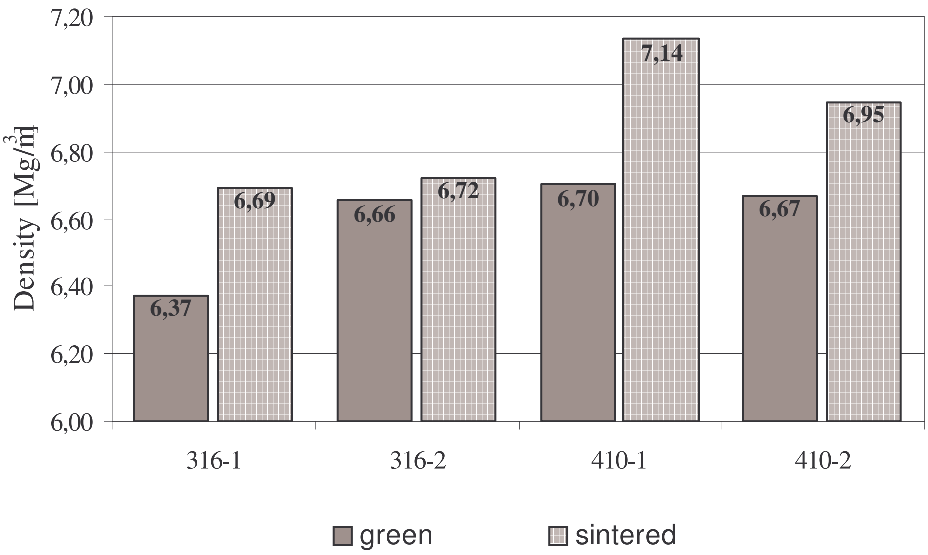


Figure 1: Green and sintered density of studied compositions

As for the martensitic based mixtures, densities were in accordance with the previously mentioned results [3,7,8] and were included in the range of 6,9 to 7,15 Mg/m^3.

For the 316L based powders, instead, lower values were obtained, even though starting with green values similar to the other compositions. It is remarkable to notice that, in case of mixture 316-2, an approximate dimensional stability was obtained.

The following microstructures, referring to compositions named 410-2 and 316-1, show the presence of a fine microstructure with no recollection of precipitates.

Austenite and ferrite are strictly compenetrated with an observed balancing between the two structures present throughout the sample.

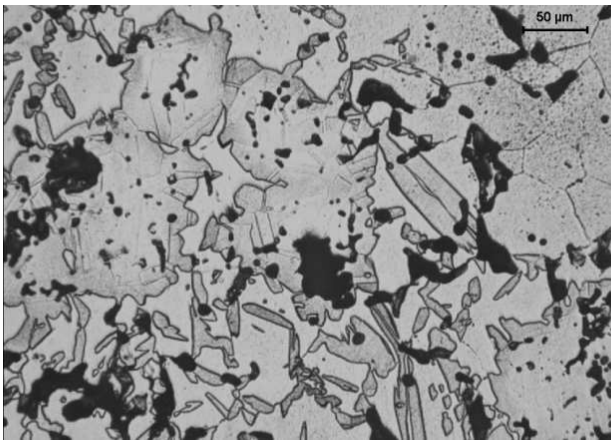


Figure 2: Microstructure of sample 410_2

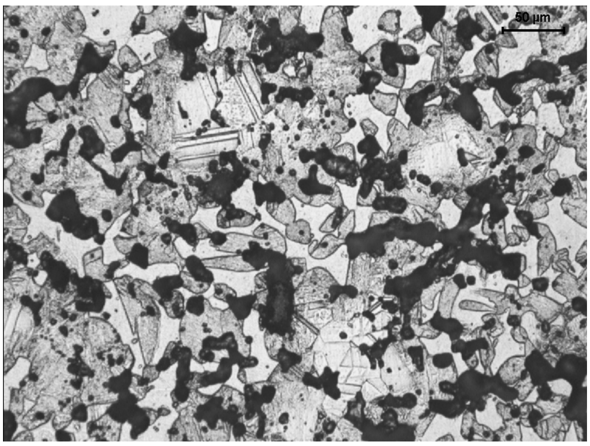
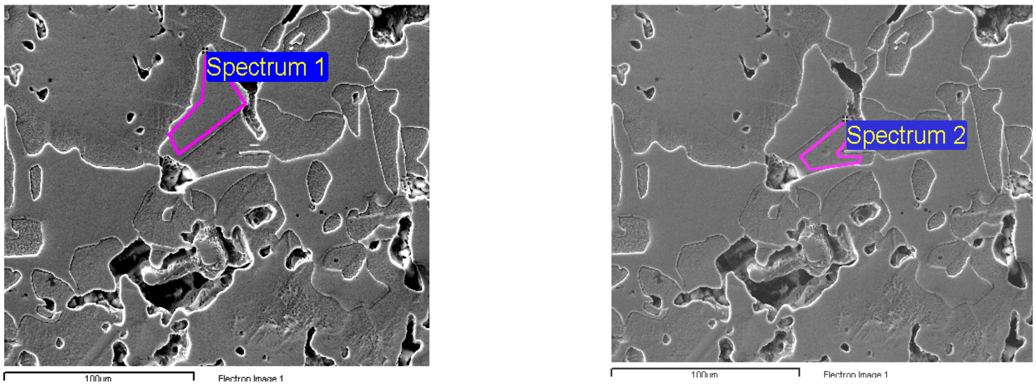


Figure 3: Microstructure of sample 316 –1

SEM analysis were carried out in order to further investigate the elements distribution throughout the structure. The following figures give an example of the obtained results.



Analisys	Elements					
	Cr	**Ni**	**Cu**	**Mo**	**Si**	**Fe**
Spectrum 1 [wt %]	31.70	4.39	--	3.73	--	60.17
Spectrum 2 [wt %]	24.00	7.61	1.58	2.16	0.76	63.89

Figure 4 : Example of SEM/EDS analysis carried out on 410-2 composition. Results in terms of the elements wt. % refer to the marked areas

The presented analysis underlines the compenetration of the austeno-ferritic grains; it is evident that, within few microns, a relevant change in the composition is achieved; similar results were also obtained for the other investigated compositions.
The corrosion tests, carried out in salt spray chamber and in a solution 0.5 M of sulphuric acid at room temperature, put into evidence a good performance of the tested samples, especially if compared to more traditional stainless steels.

CONCLUSIONS:

The first results deriving from this approach in sintering seem to be very promising for obtaining a balanced duplex structure. The use of elemental powders added to a stainless steel base showed its potentialities, in terms of fair compressibility and final sintered density. In addition a good structural homogeneity was achieved, also working with cycles possible for industries. Therefore it can be said that the way for further deeper analysis and, most of all, for the final industrialisation of the process/product is traced.

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