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High density sintered stainless steels with improved properties

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ABSTRACT

Purpose: of this paper is the study of the properties of sintered AISI 316L (1.4404 according to EN 10088. Sintered stainless steels occupy a prominent position in the high alloyed steels, however their properties are limited by the presence of porosity. The improvement of quality and performances of products coupled with a reduction of manufacturing costs calls for high compacting pressures, as well as high sintering temperatures. However, the possibility to fill the open porosity of sintered parts by infiltration process with a metal alloy or by the use of reactive sintering techniques can favour the production of stainless steel parts with enhanced mechanical properties and good corrosion resistance).

Design/methodology/approach: Sintered AISI 316L (1.4404 according to EN 10088) stainless steel samples have been manufactured using different combinations of compacting pressure and sintering parameters (time, temperature, atmosphere), or a modified composition able to allow reactive sintering process, as well as the contact infiltration with bronze.

Findings: The studies have been forwarded towards the statical and dynamic mechanical properties, as well as the corrosion behavior. Lowering the porosity level and increasing the sintering degree, by use of higher compacting pressure or sintering temperature, is of great effectiveness, especially from the point of view of mechanical properties and fatigue endurance.

Practical implications: the obtained results demonstrate the benefits of contact infiltration and of reactive sintering techniques to sinter stainless steels components having higher density and better mechanical and corrosion resistance properties than the traditional compositions, compacted at high pressure and sintered at elevated temperature.

Originality/value: very promising results have been also obtained with a modified composition able to allow reactive sintering process.

Keywords: Stainless steel; Reactive sintering; Contact infiltration; Corrosion resistance; Density

1. Introduction

Sintered components are gaining more and more applications, their success towards the most traditional technologies is due to the possibility of low cost manufacturing of parts having complicated shape coupled with restricted tolerances, to the very high yield of the utilisation (>95 %) of the raw material, as well as to the availability of a large choice of powders with a wide range of chemical composition.

The number of available compositions of alloyed iron powders allows the design and the manufacturing of parts having very high performances and among the different materials stainless steels occupy a prominent position. However, porosity, beside the mechanical properties, tends to reduce the corrosion resistance properties of components and many efforts are in course in order to reduce the porosity level of sintered stainless steels.

The challenge of the industrial production is toward the improvement of quality and performances of products coupled with a reduction of manufacturing costs. These requirements frequently are in contrast, in particular high performance sintered parts usually require high compacting pressures for the powders, as well as high sintering temperatures for the green compacts. Even if with the traditional compositions is possible now a day obtain stainless steel parts with good mechanical properties and corrosion resistance [1, 2], the researches are aimed towards new compositions able to allow enhanced properties without the requirements of high compacting pressure or of expensive technologies [3, 4].

The modification of the powders composition by addition of elements (such as copper, boron, phosphorus) favouring liquid phase sintering, as well as reactive sintering processes given by nickel additives, are matter of well developed studies [5]. Nevertheless, adopting contact infiltration techniques to fill the pores with a liquid metal the steels properties are highly improved, maintaining at the same time good dimensional control [6]. Reactive sintering processes demonstrate the possibility to manufacture stainless steel sintered parts with restricted dimensional changes, very high density values and good corrosion resistance.

This paper deals of the properties of sintered AISI 316L (1.4404 according to EN 10088) stainless steel samples, manufactured using different combinations of compacting pressure and sintering parameters (time, temperature, atmosphere), as well as the contact infiltration process. Moreover, very promising results have been also obtained with a modified composition able to allow reactive sintering process.

Besides the density, the hardness and the tensile mechanical characteristics, as well as the corrosion resistance properties, the attention has been directed towards the dynamic and the fatigue behaviours. In fact, the use of structural sintered parts under cyclic loading conditions becomes more and more important and stimulates an intense research activity to better understand the influence of the porosity on the fatigue behaviour of sintered components and to improve their fatigue strength [7]. From this point of view, the control of the level and of the shape of pores is very important, because the morphology of the porosity controls the opening and the propagation of fatigue cracks. It is possible to improve the fatigue life through the sintering process, as well as by means of suitable heat treatments.

2. Experimental part

Water atomised AISI 316L powder has been used to produce the sintered samples. The apparent density of the powder was equal to 2.79 Mg/m^3 and its chemical composition as wt. % was: Cr=16.78; Ni=13.48; Mo=2.0; Si=0.77; Mn=0.11; C=0.02; O=1900 ppm; N=520 ppm; Fe=bal.. In order to reach the reactive sintering process the composition of the AISI powder has been modified adding in different amounts Ni, Fe, Cu and Al, the exact quantities are confidential. The powders have been mixed with solid lubricant, namely 0.75% Acrawax, and compacted at 500 or 700 MPa to produce tensile samples (Standard ASTM E8-89, cross section 5.9x5.6 mm) and impact samples (dimensions 55x10x10 mm).

In table 1 the groups of tested samples are indicated together with their manufacturing process. After the dewaxing stage in nitrogen atmosphere (1h at 600 °C), the samples have been sintered in an industrial vacuum furnace with nitrogen backfilling or in a laboratory tubular furnace with pure hydrogen atmosphere at different temperatures, the reactive sintering process (type E samples) has been done in pusher type industrial furnace with nitrogen-hydrogen atmosphere. The samples type D have been contact infiltrated with copper-tin (10% tin) alloy, using enough quantity of alloy to fill 90% of the porosity at least.

The green density and the density of sintered samples were measured by water displacement method.. On the sintered specimens the hardness properties as well as fatigue, impact and tensile properties were measured. Finally the corrosion resistance of the sintered samples was tested by measuring their mass losses after increasing immersion periods (7, 14, 21 and 28 days) in 0.5 M sulphuric acid solution. The porosity and the microstructure characteristics of the sintered samples were analysed by means of light microscope and of scanning electron microscopy observations.

3. Results and discussion

The sintered density and the measured mechanical properties are listed in table 2, the green density of the samples type A, B and C was 6.43 and 6.75 Mg/m^3 corresponding to the compacting pressure of 500 or 700 MPa, whilst was 6.92 for samples type E, being higher the compressibility of this modified mixture.

The properties of samples type B and C are very similar, the increase of sintering time from 30 to 60 minutes at 1150°C does not allow significant advantages, while the other samples (type A, D and E), even if with different motivations, show better properties. The contact infiltration process causes very high increments of mechanical properties and excellent ductility, even if the powders were compacted at 500 MPa only and the compacts were infiltrated and sintered at lower temperature (0.5 h at 1150°C) than samples type A and E. The reactive sintering process appears to be advantageous when compared with traditional sintering, however there is no substantial difference of properties with respect to contact infiltration, exception made for higher ductility characteristics as can be observed comparing the values of the elongation % and of the unnotched impact energy.

All fatigue tests have been carried out in plane bending (stress ratio $R = -1$) using a Schenck PWO testing machine with 30 Nm maximum moment and 25 Hz maximum frequency. About 30 specimens have been tested for each group of samples, carrying out tests under stress levels above the fatigue limit to determine the Wöhler curves.

The fatigue curves for the different series of samples are shown in figure 1 and include the fatigue limits at 10, 50 and 90% probability of survival (solid lines), and the lower 95 % confidence limit of the latter (dashed line). The isolated points on the diagrams correspond to the raw data, each cross indicates a failure and each circle a runout. The fatigue properties of samples type B and C as already observed for the other characteristics are comparable and in figure 1 only the fatigue curves of type C samples are plotted.

The poor fatigue properties of these samples are evident, while samples type A (compacted at 700 MPa and sintered 1 hour at 1250 °C) show higher fatigue strength. The infiltration process, as well as the reactive sintering appear to have very positive effects on endurance behavior too, in fact fatigue properties of samples type D and E are comparable with those of samples type A. Considering the fatigue limits at 50 % of survival as a function of the density of the specimens, it seems that the limit of density for good fatigue behaviour is around 7 Mg/m^3, while the increase sin density at higher values, as in the case of infiltrated specimens or of the samples obtained by reactive sintering, does not allow to significant advantages. This means that there is a level of porosity under which the fatigue behaviour and the tensile strength will be controlled mainly by the mechanical properties proper of the material rather than by the porosity .

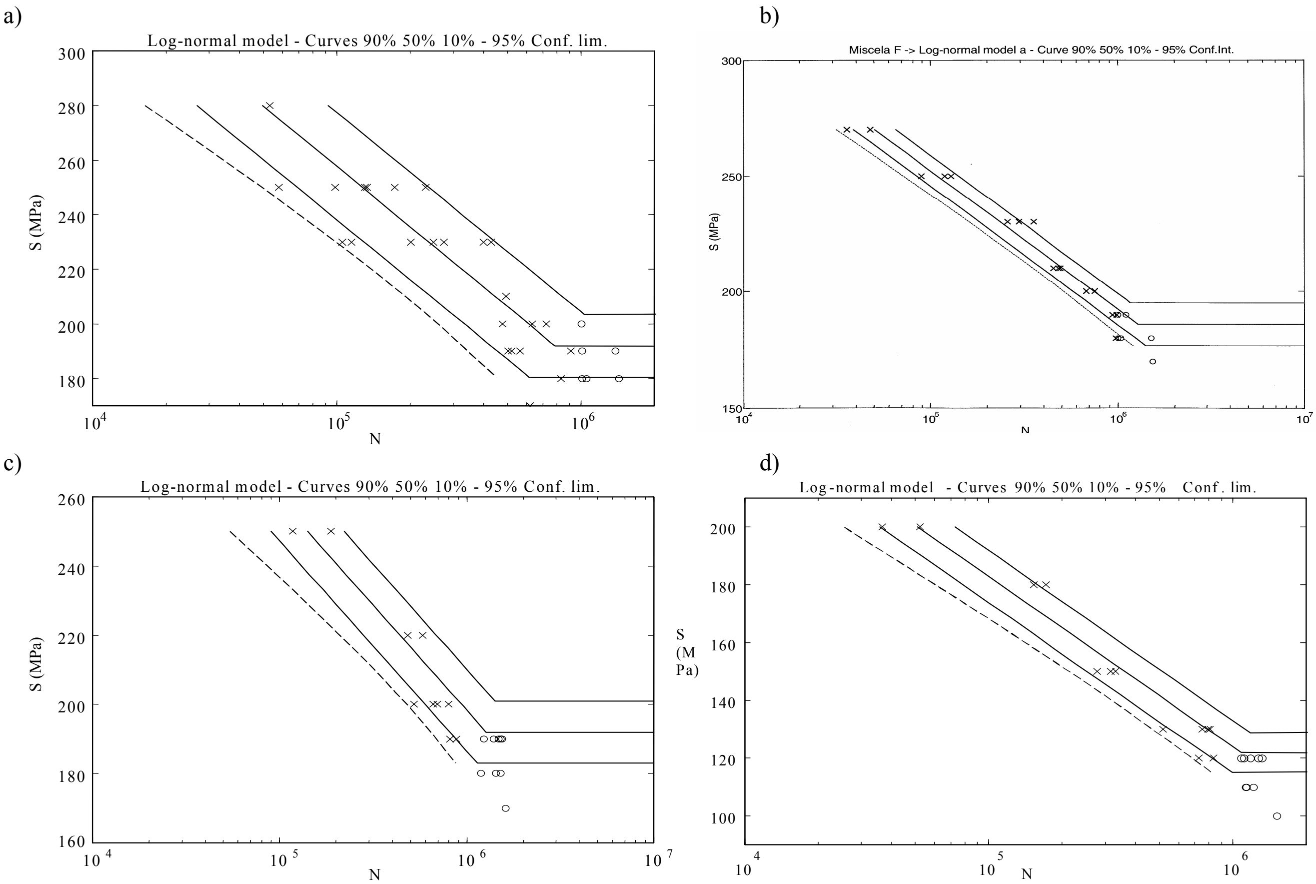

Fig. 1. SNP curves for type A, C, D and E samples

Table 1.
Compacting pressure, temperature, time, furnace atmosphere and additional parameters

Sample	Pressure [Mpa]	Temp. [°C]	Time [min.]	Atmosphere
A	700	1250	60	Vacuum + Nitrogen backfilling
B	500	1150	30	Hydrogen
C	500	1150	60	Hydrogen
D	500	1150	30	Hydrogen + C.I.
E	700	1275	30	50% Hydrogen + 50% Nitrogen

Table 2.
Density, tensile properties, unnotched impact strength and harness of samples

Sample	Density [Mg/m^3]	Yield strength [MPa]	U.T.S. [MPa]	Elongation [%]	U.I.S.[J/cm^2]	[HRB]
A	7.05	361	549	14	73	77
B	6.59	170	270	8	30	31
C	6.70	175	287	12	44	34
D	7.45	290	540	30	100	64
E	7.45	350	510	24	130	63

While in the wrought materials the presence of defects (inclusions, precipitates and geometrical notches) represents the sites for cracks nucleation, in the sintered materials pores are additional zones for stress concentration and the related stress intensity factors are difficult to determine and pores appear to be like cracks precursors. Several studies have found that in sintered materials cracks originate after few cycles, usually the pores are the precursors of the cracks that originate from them. Moreover, the distance between pores and their radius are the dominant parameters .

The observation of the microstructure highlights the influence of the morphology of the porosity on the fracture propagation: pores can put out cracks, but can constitutes zones of high stress intensity, favouring the initiation of a new fracture process which propagates through the matrix.

Generally cracks propagation follows the pores textile, however the reduction of the porosity by infiltration process obstacles fracture process and improves the response of sintered materials to fatigue process, in the same way acts reactive sintering.

In figure 2 the fracture morphology of samples type B and D are compared. The type B samples compacted at 500 MPa and sintered 30 minutes at 1150 °C show, in the as sintered state, high porosity degree and reduced sintering grade, while the infiltrated specimens (type D) show a microstructure and a fracture surface typical of a liquid phase sintered system. In fact, the grains of steel are surrounded by the infiltrant alloy and this justifies the highest ductility, being evident the large deformation degree of this phase due to the fracture process. A few residual pores are sometimes present, however the adhesion between the steel matrix and the infiltrant alloy appears very good and continuos. The porosity observed in type B samples explains their low fatigue strength. This feature can be justified by the different morphology of the pores that are not as rounded as in the infiltered samples so that their action as fracture precursors is emphasised. The fatigue cracks are nucleated from the surface, propagate inwards, reach the pore and restart.

In figure 3 the SEM analysis performed on the fracture surface, as well as on a polished section of type A specimens highlights the morphology of some porosity and of fracture surface. Brittle and ductile fractures coexist in different amounts and secondary cracks between grains can be observed (fig. 3A). The microstructure of these samples is characterised by the precipitation of Cr nitrides at grain boundary as can be observed on the SEM microphotograph in fig. 3B.

The SEM observation of fracture surface of samples obtained by means of reactive sintering (type E) highlights the presence of some round shaped intermetallic particles (figure 4A), the general aspect of the fracture show a ductile behaviour, even if correspondingly to the intermetallic compounds the morphology of the fracture appears as a quasi-cleavage type.

In figure 4 B the SEM microphotograph highlights the presence of the intermetallic compound at the boundary of grain, where it fills the former empty space between the stainless steel particles and close down the porosity channels. EDS microprobe was helpful to analyse the chemical composition of the compound: close to the austenitic matrix of the steel (zone 1) the concentration of Al is about 20 wt% and it tends to increase towards the centre of the particle, reaching the highest value of about 31 wt%. Probably the central layer of the compound is constituted by (Fe,Ni)Al, while in the external part $(Fe,Ni)_3Al$ could be present, because it is the thermodynamically favourite one [4]. It was formed near interface between Al particle and the other metallic ones: so the compound acts as barrier diffusion and it prevents the total reaction of Al. In the left part of the compound there is a pore: its presence can be due to the Kirkendall effect.

The corrosion resistance of the sintered samples is dependent upon their porosity and their chemical composition. The histogram of figure 5 shows the mass losses of the studied samples weekly measured after their immersion in 0.5 M sulphuric acid solution at room temperature. The corrosion rates of samples type A, B and C are comparable but with different motivations. In fact, the precipitation of chromium nitride on the samples sintered in vacuum at 1250 °C with nitrogen backfilling (type A) causes Cr depletion of the matrix and consequently a decrease of the corrosion resistance, while in the specimens (type B and C) sintered in hydrogen the corrosion is determined mainly by the high degree of porosity, in this case the decrease of weight loss during the fourth week more than to a passivation phenomena may be due to the filling of pores with corrosion products.

The infiltrated samples show very high corrosion resistance because of the quasi absence of porosity, filled with Cu-10%Sn alloy, moreover sintering in hydrogen atmosphere avoided also any Cr depletion phenomena. Whilst in the case of type E samples, even if characterised by very low porosity and high density, the corrosion rate is higher than for the infiltrated ones because the sintering process was performed in nitrogen containing atmosphere with possible Cr depletion. However the process, with respect to the samples type A, B and C, starts with lower rates, these progressively increase probably due to the effect of intermetallic compounds.

The obtained results fit very well with studies performed on the impact strength and energy absorption during crack initiation and propagation on the same steel grades. Moreover, developing studies related to innovative duplex statinless steels compositions very excellent and unique results were obtained [8]. The properties highlighted by the developed innovative compositions are difficult to reach using more traditional stainless steel grades [9-13]. However, the high mechanical strength and corrosion resistance properties of the innovative compositions were also obtained thank to the use of vacuum or of hydrogen based atmospheres during sintering and providing a fast cooling step after the sintering process. These kind of atmospheres, more than other sintering aids, are always the most convenient way to produce stainless steel parts with very good properties.

4. Conclusions

The sintering processes and the properties of sintered AISI 316L (1.4404 according to EN 10088) stainless steel have been studied on samples characterised by different porosity level, due to different compacting pressures and sintering conditions, as well as to the application of infiltration process or of reactive sintering technique. The studies have been forwarded towards the statical and dynamic mechanical properties, as well as the corrosion behaviour.

Lowering the porosity level and increasing the sintering degree, by use of higher compacting pressure or sintering temperature, is of great effectiveness, especially from the point of view of mechanical properties and fatigue endurance.

b) d)

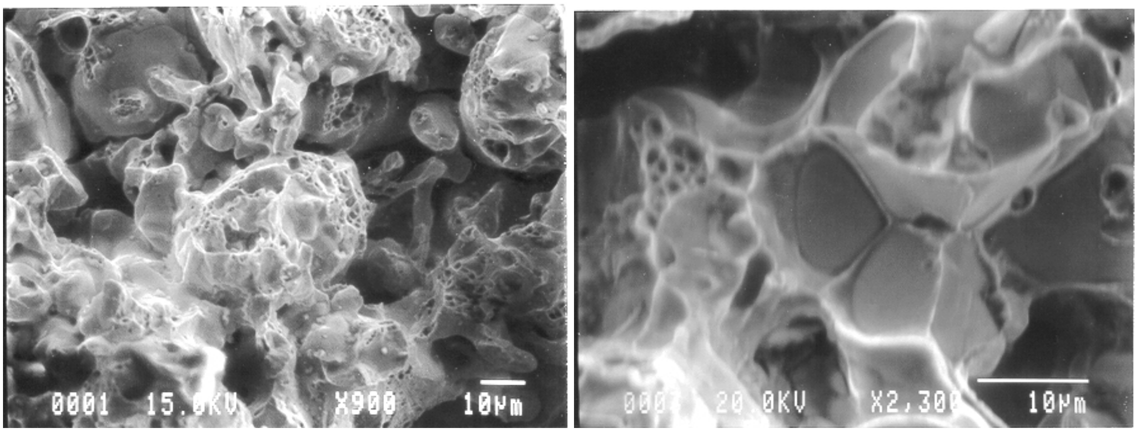

Fig. 2. Fracture morphology of type B and type D samples after impact test

a) b)

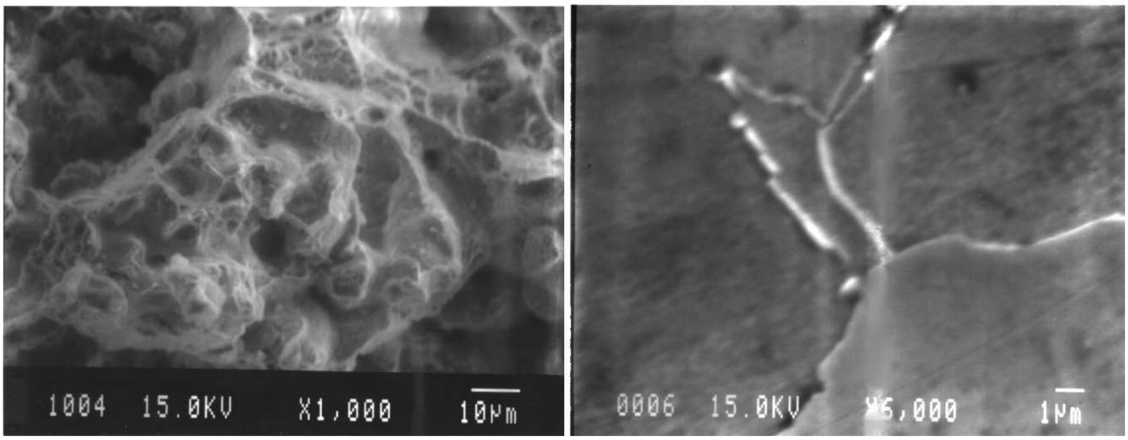

Fig. 3. Fracture morphology of type A samples, after impact test (A) and Cr precipitates at the grain boundary (B)

a) b)

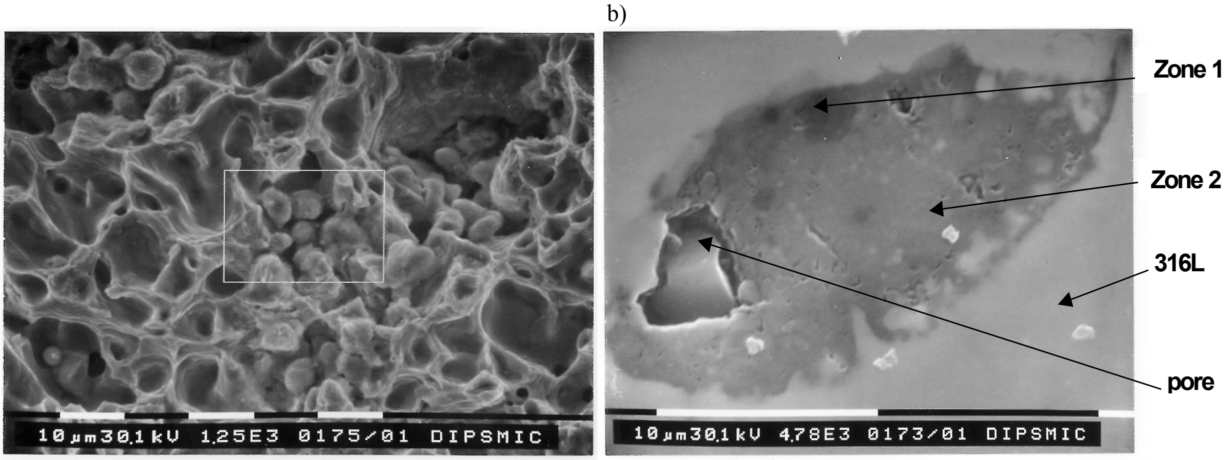

Fig. 4. Type E samples: morphology of fracture surface (A) and SEM micrograph of a an intermetallic compound (B)

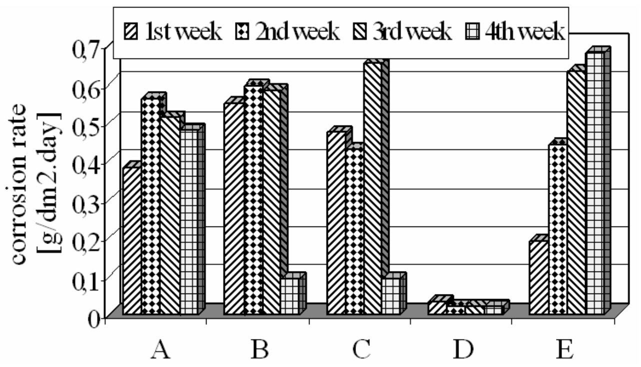

Fig. 5. Corrosion rate in 0.5 M sulphuric acid solution of studied samples

The reactive sintering process is able to enhance densification, to reduce the total and open porosity and to guarantee high density levels with properties comparable with those of the samples having the traditional composition and sintered at the highest density.

The contact infiltration process with Cu-Sn alloy applied to low density green compacts (compacting pressure only 500 MPa) and sintered at 1150 °C for 30 minutes only, is suitable to reach properties at least equal or higher than those of samples compacted at 700 MPa and sintered 60 minutes at 1250 °C or of modified samples for reactive sintering.

The corrosion resistance is favoured by low porosity and by the absence of precipitation of intermetallic compounds or of phases, like chromium nitrides, which cause Cr depletion of the matrix.

Contact infiltration is tremendously advantageous from the point of view of the corrosion resistance properties, while reactive sintering allows the highest ductility characteristics.

Reactive sintering and contact infiltration represent valid routes to manufacture high density and resistant stainless steel components. Moreover, the infiltration process constitutes an economic and reliable alternative to high compacting pressure and high temperature sintering processes.

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