

Microstructure and Properties of Hybrid-Alloy Chromium Steels

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ABSTRACT

Price fluctuations and environmental issues have driven the development of new ferrous PM alloys towards chemical compositions that more closely match those of wrought steels. In particular, the use of Cr combined with lesser amounts of Mo and Ni allows PM steels with excellent combinations of dimensional stability and mechanical strength to be developed. In order to obtain optimum properties, and to guarantee proper oxide reduction and strong necks between particles, sintering must be carried out under suitable conditions of atmosphere, temperature and time. This paper discusses the sintering, hardenability, microstructural characteristics and properties of hybrid low-alloy chromium PM steels (Ancorsteel 4300) under a wide range of sintering temperatures, with special emphasis on high temperature sintering (HTS). It is shown that these high performance PM steels exhibit very attractive tensile strength and ductility when properly selected sintering conditions are used.

INTRODUCTION

Cr-Mo-Ni steels, with AISI classification series 43xx or 47xx, are well known in ingot metallurgy for the production of structural parts for highly demanding applications. They enjoy an excellent combination of fatigue resistance, wear behaviour, strength and attractive hardenability that has gained them the pseudonym of “all round steels” [1]. Although Mo and Ni, due to their low oxygen affinity, have been widely used in PM as alloying elements to Fe, chromium-containing steels are relatively recent [2-4]. Although chromium has a higher oxygen affinity, in diluted form within the chemical composition of water atomised pre-alloyed powders, it has been demonstrated that the oxide formed only contains up to 18% Cr [5] and is consequently reducible during sintering in adequate N₂-H₂ atmospheres [6]. An alternative and most interesting approach for introducing Cr, based on the use of a Master Alloy, has been uniquely identified by Hoeganaes Corporation for the design of Ancorsteel 4300. This approach is also aimed at preserving the compressibility of the [Fe, Mo]-based powder which is usually degraded by solid solution hardening in Cr-containing pre-alloyed powders. An important aspect to emphasise, apart from the aforementioned atmosphere quality, is that the sinter-hardening PM steel grades prepared from Ancorsteel 4300, and its leaner version Ancorsteel 4300L, require adequate sintering temperatures and times so the optimum microstructure, hence properties, can be properly developed [7]. As shown in the present paper the design of these hybrid sinter hardening PM steels, which consist of a mixture of prealloyed [Fe-Mo] powders with Ni, Cr, Si and graphite as alloying additions, is based on a thorough understanding of diffusion phenomena and diffusion paths for every alloying element present in the powder mixture. Paying special attention to ecological and economical aspects the selection of the chemical composition and alloying method was also aimed at obtaining maximum performance with minimum amounts of alloying elements. As previous works of the same authors

reporting on properties are available [2, 8] the present paper will be mainly concentrated on microstructural development.

EXPERIMENTAL PROCEDURE

Premixes of Ancorsteel 4300 with 0.7% graphite were made for obtaining sintered PM steels with chemical composition as indicated in Table I. Green compacts were invariably produced by uni-axial pressing for reaching a density of $\sim 7.1 \text{ g/cm}^3$.

Table 1.- Nominal compositions of the alloy.

ID	Fe (wt.%)	Mo (wt.%)	Cr (wt.%)	Ni (wt.%)	Si (wt.%)	C (wt.%)
Ancorsteel 4300	Bal.	0.8	1.0	1.0	0.6	0.6

The laboratory specimens were sintered in a batch furnace for 15 or 30 minutes at, either, 1120, 1160 or 1240 °C in an atmosphere of 90N₂-10H₂ (vol %). For studying the microstructural development during sintering a group of interrupted sintering experiments consisting of heating at 20°C/min to the sintering temperature followed by immediate water quenching were also carried out. These experiments were performed, both, as a function of temperature without holding period, and after different holding times at constant temperature. Additionally a dilatometer instrumented with controlled gas-cooling-facilities was used for obtaining the continuous cooling transformation curves (CCT diagrams) for the developed PM steel. In this equipment the imposed changes in temperature in a specimen and the respective changes in length are simultaneously recorded as a function of time. The recorded cooling curves were plotted in a temperature versus log time coordinate system, with start-time taken at the sintering temperature. For all dilatometer runs specimens in the shape of pins 6 mm in diameter, 10 mm long, were induction heated in Argon to 1120°C, held at temperature for 15 min and cooled at constant cooling rates between 34 and 0.08°C/s. Die pressed green compacts were directly used in several experiments, although, in selected cases and for the sake of completion green pins were pre-sintered in 90N₂-10H₂ at 1240°C for 15 min prior to testing in the dilatometer.

The specimens were metallographically examined under the Optical microscope as well as in the SEM and the apparent hardness of the sintered materials was measured using Vickers 30Kg (HV30).

RESULTS AND DISCUSSION

Figure 1 shows two CCT diagrams for the same PM steel after different processing conditions, firstly, after sintering in the dilatometer at 1120°C for 15 min and secondly after furnace sintering at 1240°C for 15 min prior to sintering in the dilatometer at 1120°C for additional 15 min. The corresponding microstructures from specimens cooled at a constant rate of 3.75°C/s are also shown.

Comparing the two CCT diagrams allows realising that both processing conditions yield a combination of bainite and martensite at the side of low cooling rates and martensite at faster cooling rates. The critical cooling rate is however somewhat higher ($>3.75 \text{ °C/s}$) after single processing at 1120°C whereas HTS allows obtaining nearly fully martensitic steels after cooling rates below 3.75°C/s. This is confirmed by the microstructures included in the Figure which additionally show a better developed microstructure after HTS. This is revealed by decreased compositional gradients (areas

with different contrast have been reduced and are more evenly distributed), fewer pores and the higher sintering degree shown by the generally more uniform distribution of well developed necks. In addition to this, it must also be emphasised that comparison of specimens cooled at the same cooling rate (see Figures 1 a and b) reveals that the apparent hardness (HV30), is systematically higher for those after processing at 1240°C.

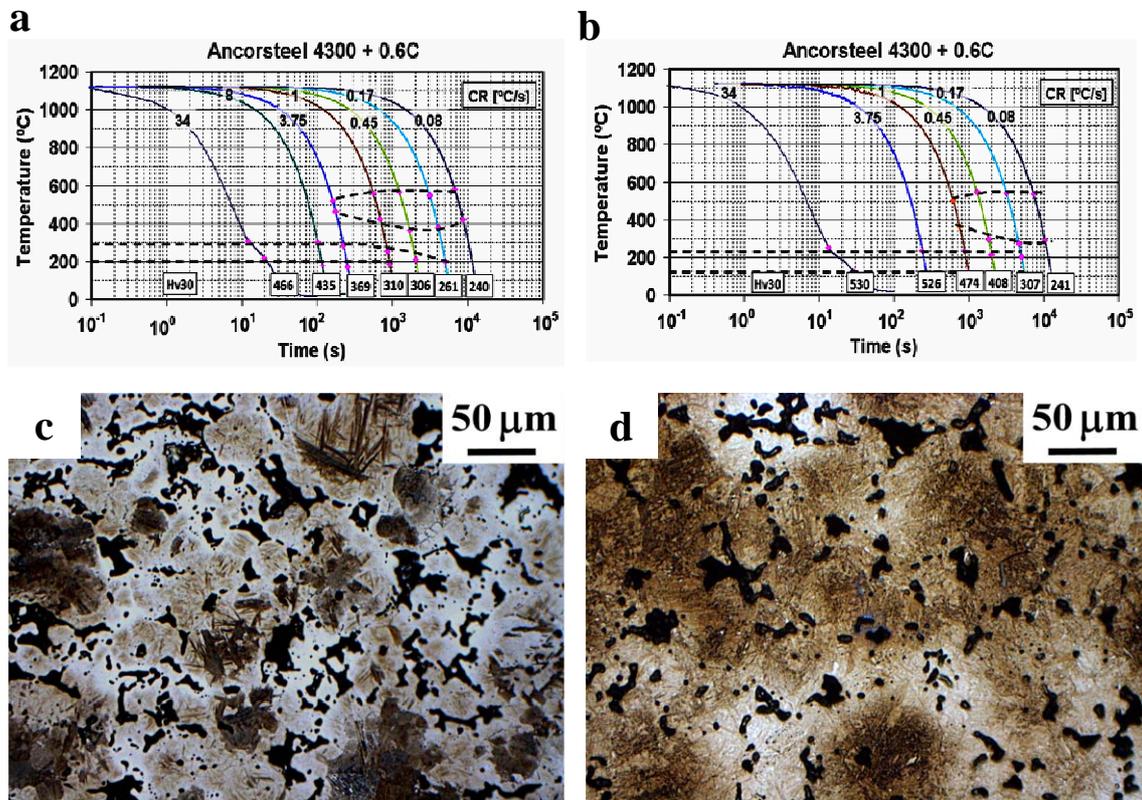


Figure 1.- CCT diagrams at 1120°C for 15 min for Ancorsteel 4300: (a) green compacts and (b) pre-sintered specimens at 1240°C for 15 min before dilatometry. Corresponding microstructures from specimens cooled at 3.75°C/s: (c) processed at 1120°C and (d) pre-sintered at 1240°C followed by dilatometry at 1120°C.

These observations indicate that the more intense material transport taking place under the thermal activation provided by HTS, in addition to the second treatment at 1120°C, the diffusion events allow better developing the alloy than by a single process at 1120°C for 15 min. This may be an obvious and expected conclusion but it emphasises the need of properly selecting the sintering cycle for these alloys since, by its alloy design, adequate combinations of time and temperature are recommended in order to obtain the attractive properties reported for these steels [2, 8].

In order to understand microstructural and hence properties development a set of optical micrographs are presented in Figure 2 corresponding to interrupted sintering cycles followed by water quenching, either, directly after reaching the sintering temperature or including a holding period at 1120°C. The sequence of microstructures captured upon reaching the sintering temperature (Figs. 2 a, b and c) allow identification of Ni particles (labelled as Ni in red), the Cr-containing Master Alloy particles (labelled as MA in light blue) and inter-diffusion areas (labelled as IA in yellow). As shown elsewhere [9] alloying when nickel is added in elemental form to any Fe-based powder follows a sequence given by: the sintering of neighbouring Ni-particles at around 900°C, surface diffusion around Fe-based particles at higher

temperatures, fast diffusion through the austenite grain boundaries of the Fe-based particles, and ending up with Fe-Ni inter-diffusion with preferential diffusion of iron into nickel.

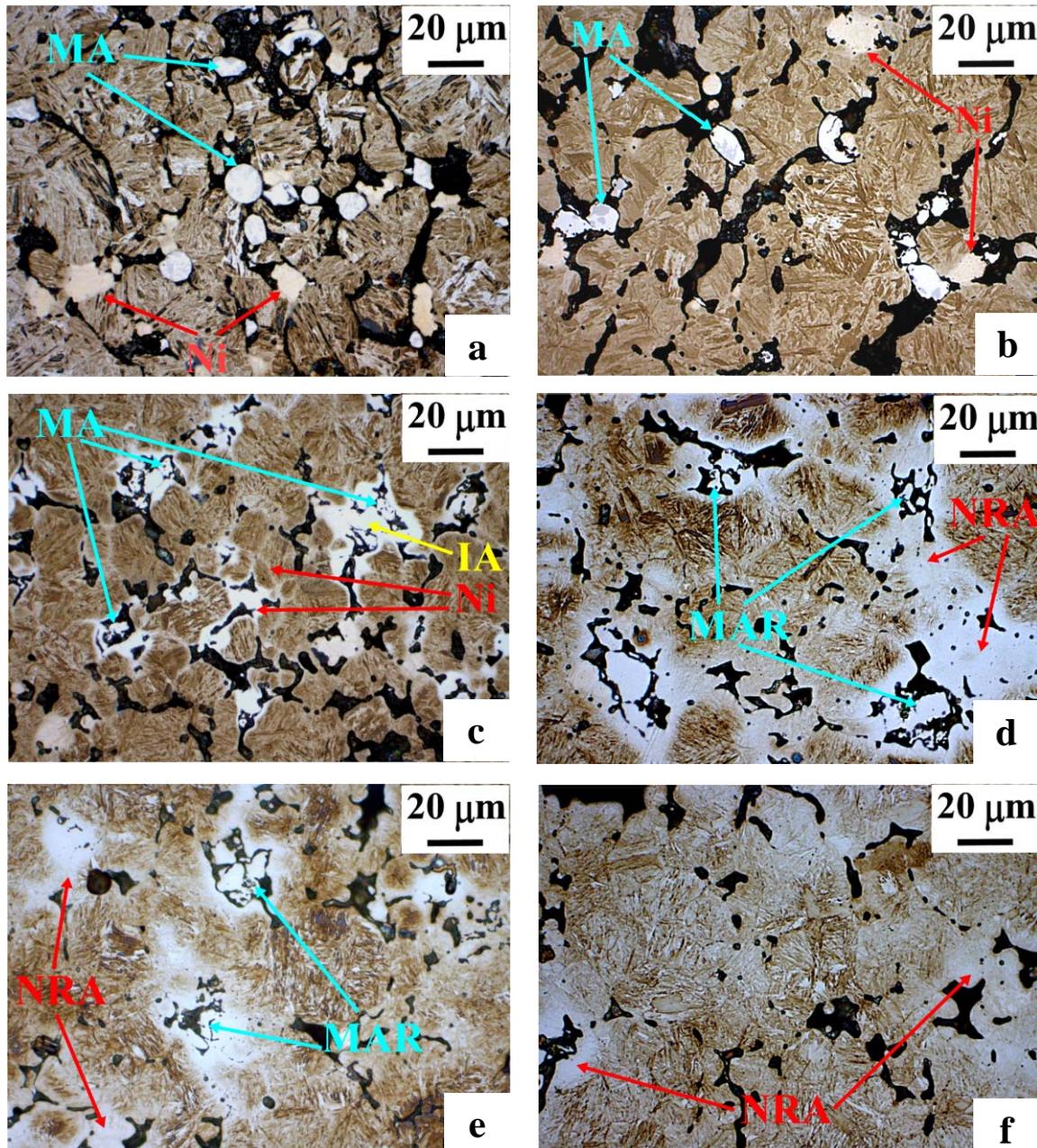


Figure 2.- Microstructures from interrupted sintering cycles followed by direct water quenching from: (a) 1050°C, (b) 1100°C, (c) 1120°C, and from 1120°C after: (d) 5 min, (e) 15 min, and (f) 30 min.

These events may be identified in the aforementioned microstructures up to 1120°C. Although the Ni-particles are neatly recognised, both, at 1050°C and at 1100°C it is noticeable that they have lost their typical Ni-carbonyl appearance. At 1120°C it is clearly shown that the grain boundaries of the Fe-grains are decorated thus leading to the typical fragmentation [9, 11] of the Fe-based particles. During the same sequence the Cr-containing MA-particles are still quite recognisable, either, still preserving their original shape and chemical composition (Figs. 2 a and b) or as porous remnants after partial reaction with surrounding nickel (Fig. 2c). Another function fulfilled by nickel is

allowing redistribution of other admixed alloying elements, therefore, at 1120°C where a noticeable increase of alloying activity is evidenced the formation of MA-nickel inter-diffusion areas (IA) also incorporating Fe-Mo-C contributes to microstructural development. As noticed in Figs. 2 d, e and f, time at temperature now allows changes in the incipient IA areas to be converted into Ni-rich areas (NRA) which are progressively enlarged due to the incorporation of Fe-Mo-C by bulk diffusion from the prealloyed Fe-based particles. Although after 15 min several MA particles remnants (MAR) are still evident the chemical gradients gradually tend to be smoothed out. After 30 min (Fig. 2f) the preferential diffusion of Fe into Ni from the Fe-grains (along with Mo and C as mentioned above) causes the dilution of those Ni-Rich-Areas to the extent of locally generating a variety of Ni-containing steels capable to transform into martensite upon cooling. After water quenching not only those more alloyed regions (which obviously enjoyed increased local hardenability) will transform to martensite but also the Fe-Mo-C grains. As a consequence the microstructure in Figure 2f exhibits extended martensitic regions. It is also evident that those regions where the concentration of Ni may still be too high (either, because of an agglomeration of Ni-particles or simply due to lack of time) will remain as untransformed austenite. These are labelled as NRA in Figure 2f.

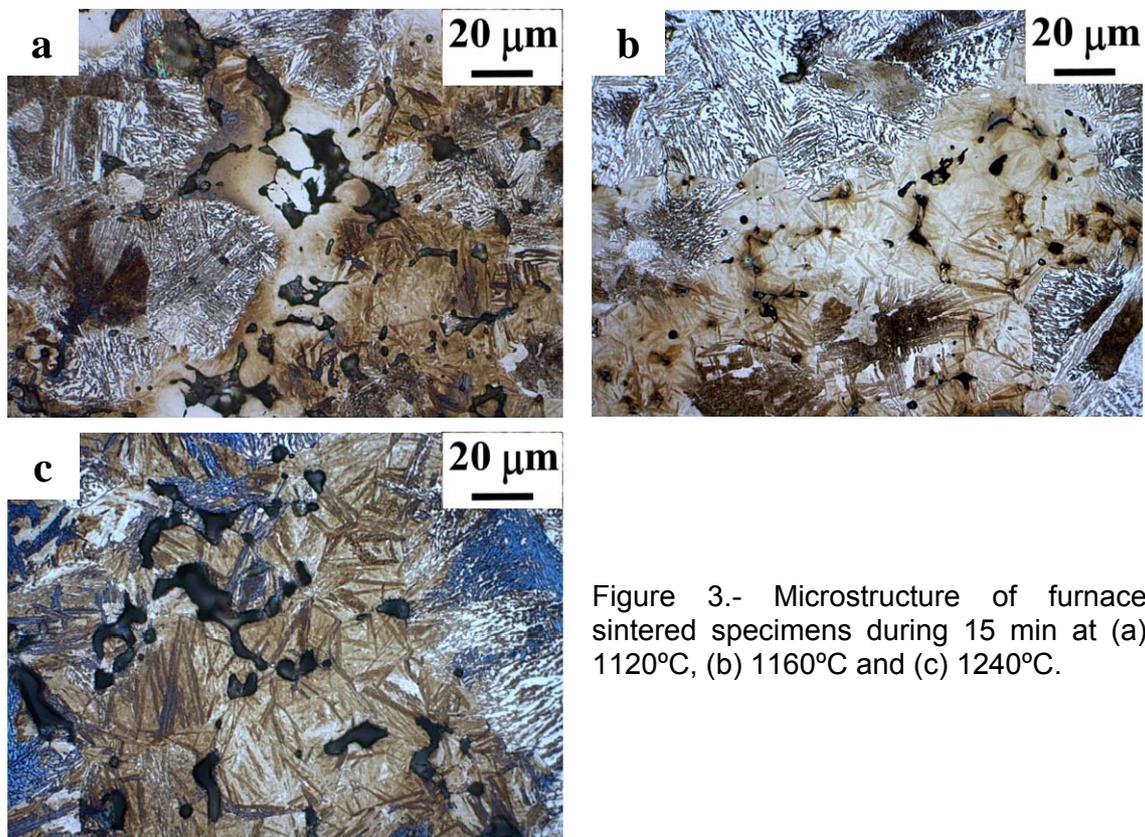


Figure 3.- Microstructure of furnace sintered specimens during 15 min at (a) 1120°C, (b) 1160°C and (c) 1240°C.

On the other hand as specimens are furnace sintered and cooled at conventional cooling rates (around 0.45°C/s) only the alloyed areas with local high hardenability will transform to martensite as predicted by the CCT diagrams. Figure 3 shows the microstructures of furnace sintered specimens for 15 min at 1120, 1160 and 1240°C which clearly consist of bainitic areas, corresponding to the Fe-Mo-C grains (that do not generally contain neither Cr nor Ni), and martensite in the Fe-Cr-Ni-Mo-Si-C regions. This argument is further supported by the results shown in Figure 4 corresponding to a specimen sintered at 1240°C for 30 min followed by conventional cooling. The SEM picture and the line scan, carried out over the red straight line in the micrograph without considering Mo and C, show that in the martensitic region (in light contrast) the lines for

Ni, Cr and Si rise above the background level indicating a higher concentration of these elements. In contrast the darker areas are recognisably bainitic and correspond to the [Fe-Mo-C]-grains. This is an indication of the difference in local hardenability due to the heterogeneous distribution of alloying elements in the microstructure of this hybrid PM steel. It also confirms the incorporation of silicon in the alloy without a tendency to form oxides.

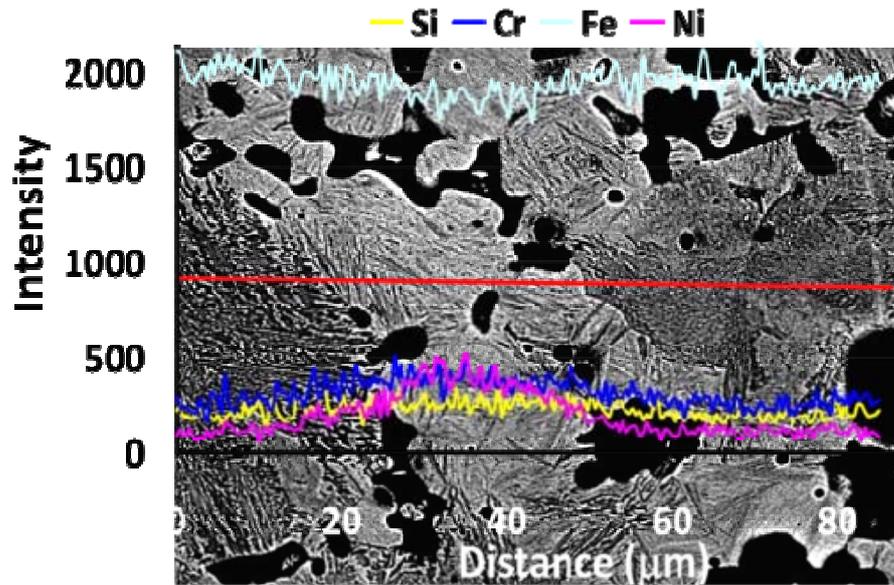


Figure 4.- SEM micrograph and line scan plot for the distribution of elements in the microstructure.

As mentioned before, this work mainly reports on the microstructural development of Ancorsteel 4300 but showing the brief summary in Table 2 highlights the attractive properties that may be achieved. Clearly these sinter-hardening PM steels exhibit an interesting combination of high yield stress with very reasonable ductility. Higher cooling rates, evidently leading to obtaining higher volume fractions of martensite, are clearly convenient for reaching maximum hardness, both, at conventional or HTS. Although HTS is evidently yielding the highest properties there are attractive values at lower temperatures particularly when longer sintering times are used.

Table 2.- Mechanical properties for PM steels sintered from Ancorsteel 4300 under various sintering and cooling conditions followed by tempering at 205°C for 1 hr.

Sintering conditions T(°C), t(min)	CR (°C/s)	σ_y (MPa)	UTS (MPa)	% E	Hardness HRC	REF
1120, 30	0.45	740	990	2.0	----	8
1120, 30	0.7	758	1007	1.7	31	2
1120, 30	2	1065	1210	1.2	30	8
1120, 30	2.2	1001	1173	1.4	39	2
1160, 15	0.45	808	1048	2.0	----	8
1240, 30	0.45	725	1061	2.8	----	This work
1260, 30	0.7	821	1145	2.5	33	2
1260, 30	2.2	1096	1489	2.5	41	2

CONCLUSIONS

Ancorsteel 4300 is a sinter-hardening hybrid PM steel with a unique alloy design that allows introducing chromium keeping the compressibility of the powder mix that contains prealloyed [Fe-Mo] particles as the basic iron powder. Silicon is also used and protected against oxidation in spite of its high oxygen affinity. As a hybrid mixture the microstructure is developed during sintering creating volumes in the compact containing higher concentration of alloying elements. Such volumes of material consequently have higher local hardenability being able to transform to martensite at relatively slow cooling rates. This paper describes the series of diffusion events leading to microstructural development which is based on the redistribution of the constituting elements aided by nickel under thermal activation and as a function of time. Interrupted sintering cycles allows acquiring a thorough knowledge of diffusion routes for each element which combined with their metallurgical role in the PM steel leads to attain markedly attractive mechanical properties. Adequate sintering time-temperature combinations are consequently recommended to reach the full potential of this PM steel. As verified from the mechanical properties HTS yields superior properties particularly coupled with an accelerated cooling rate. But lower temperatures are also convenient, preferably in the range of 1150 to 1160°C, provided time at temperature around 30 min is allowed.

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