

INFLUENCE OF CONTROLLED ATMOSPHERES ON THE PROPER SINTERING OF CARBON STEELS

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Abstract

Before explaining the meaning of the word proper in this context, the influences of carbon on microstructures and properties of wrought steels are presented. For a long time, basic metallurgical knowledge has showed that the optimum properties, depending on alloy additions, can be achieved only by a precise control of carbon content. A comparison between tolerance amplitudes on the carbon content of fully dense steel versus sintered steel is strongly unfavourable to PM. Independently from this comparison, a precise control of carbon content is always a critical factor for achieving, systematically, the highest properties. The thermodynamic bonds concerning carbon equilibria during sintering are discussed and possible interactions between steel and various controlled atmospheres are examined. The evaluation of physical properties of single gases, present in controlled atmospheres at various temperatures, shows that their behaviour and their effects may differ, even dramatically. From a chemical standpoint, some atmosphere constituents can cause carbon depletion or enrichment, whereas others do not modify the equilibria. In the case of chemical changes during sintering which involve carbon, the temperature profile in some furnace zones may be a critical item. The microstructures, after cooling, obviously depend on thermal gradients within certain temperature ranges. The requirements to be fulfilled on furnaces fed with different atmospheres, for a narrow control of carbon content and corresponding narrow tolerances of properties after sintering, are discussed. Some common schemes of equipment are analysed, and their suitability to a correct carbon and microstructure control during sintering is surveyed.

Keywords: carbon, controlled atmospheres, furnaces, properties, sintered steels.

INTRODUCTION

Over the last decades, PM parts, compared with other competing forming technologies for mass applications, enjoyed a remarkable expansion. By and large, the factors that fostered the growth include significant improvements of PM steels properties, brought on by bettered raw materials, higher compaction pressures, warm compaction, sinter hardening, and high temperature sintering. Step by step, the gap of mechanical characteristics that divides fully dense steels from the best porous ones shrinks. In a middle-term perspective, it seems not a far-fetched hypothesis to forecast that PM steels will be definitely equivalent to conventional, non-porous, ones. The affirmation of sinter forged connecting rods agrees with this statement. It should be obvious that, in parallel with the shrink of gap in the properties, the tolerance ranges of chemical composition of high-

performance sintered materials will also become, progressively, more similar to those allowed for fully dense steels. Surprisingly, any survey of the main topics investigated by scientist and PM engineers, both in academia and in industry laboratories, does not reveal any special attention or research activity aimed at the narrowing of tolerances on carbon content. This gap depends on many reasons. Any attempt to reduce the tolerance ranges of carbon of PM steels requires a refusal of deep-rooted opinions and a nearly revolutionary approach to well-established sintering processes and equipment. On this ground, it seems helpful to collect available information and to prepare a well-founded survey, suitable to favour any possible narrowing of carbon tolerances. The analysis of accessible literature and some specific approach, based on production experience, should contribute to improving industrial sintering processes and equipment, with the final result of reduced scattering on the properties of PM steels. The purpose of this report is to make the PM community really interested in technological progress, aware of the problems that could arise, in the long run, from an unjustified difference on carbon specification. This difference between specifications may explain the perplexity that several end-users still demonstrate towards high property PM steels. To be honest, such a perplexity may derive from several and rather common sintering processes, which can appear *improper* to user engineers, more used to selecting and applying fully dense steels. The misgivings will gradually disappear, as far as sintering processes and equipment will improve, becoming more “*proper*”, leading to narrowed tolerances on the carbon content of PM steels. To avoid any possible misunderstanding, it is necessary to explain first which meaning should be attributed to the word “*proper*” in the context of the present report.

Among various meanings listed by two dictionaries [1,2] the choice can be restricted to the following ones:

1. Adapted or appropriate to the purpose or circumstances; fit; suitable.
2. Strict; accurate.
3. Suitable; appropriate.
4. Worthy of the name.
5. Meeting a requisite standard of validity.
6. Rigorously correct; exact.

The consideration of fully dense steel contributes to restricting the range of choices about meanings. Their basic metallurgy underlines that the presence of carbon is an essential condition to reach high mechanical properties. Alloy additions are needed, to attain specific characteristics, but their contributions are possible and optimally exploited only if the right amount of carbon is present. Figure 1 (based on data taken from ASM [3]), shows the influence of carbon on the tensile properties of fully dense, hypoeutectoidic, plain steels, in different structural states. The corresponding equations, achieved by regression analysis, are

U.T.S. = $1284.6 \times C\% + 283.15$ MPa, with $R^2 = 0.9934$, for quenched and tempered steel;

Y.S. = $947.86 \times C\% + 253.64$ MPa, with $R^2 = 0.9977$, for quenched and tempered steel;

U.T.S. = $1022.0 \times C\% + 145.40$ MPa, with $R^2 = 0.9955$ for normalized steel, valid for $0.17 \leq \%C \leq 0.7$;

Y.S. = $297.5 \times C\% + 272.11$ MPa, with $R^2 = 0.9943$ for normalized steel, again valid for $0.17 \leq \%C \leq 0.7$.

Let us suppose that for 0.6 % nominal carbon content, the tolerance range spans from 0.57 to 0.65 %. Correspondingly, after heat-treatment, U.T.S ranges from 1015 MPa to 1181 MPa, whereas Y.S. ranges from 794 to 870 MPa, and the total scatters, with respect

to the average values, are: 15 % on U.T.S. and 9 % on Y.S. Analogously, if the tolerance range for 0.35% nominal carbon content spans from 0.32 to 0.39 %, U.T.S. ranges from 694 MPa to 784 MPa, whereas Y.S. ranges from 557 to 623 MPa and the total scatters, again with respect to the average values, are: 12 % on U.T.S. and 9 % on Y.S. Table 1 [4] lists the allowed tolerances on the chemical composition of unalloyed quality steels and Tab.2 [5] lists the allowed tolerances on the carbon content of special steels, to be used after quenching and tempering treatments. For comparison, the tolerances that the most diffused standards allow on PM steels are collected in Tabs. 3, 4, 5, [6, 7, 8, 9].

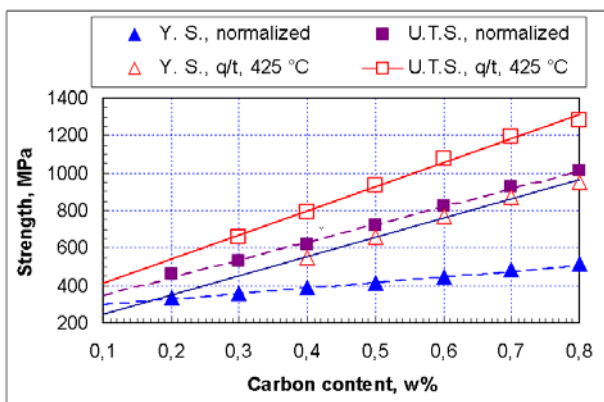


Fig.1. Influence of carbon content on tensile properties of hypoeutectoid unalloyed (wrought) steels, from ASM data.

Tab.1. Allowed tolerances on chemistry of unalloyed fully dense steels (casting analysis). UNI EN 10083, Part 2.

Type	Chemical composition, mass %									C ranges	
	C	Si max	Mn	P max.	S max.	Cr max.	Mo max.	Ni max.	Cr + Mo + Ni max.	weight %	relative %
C 22	0.17-0.24	0.40	0.40-0.70	0.045	0.045	0.40	0.10	0.40	0.63	0.07	34.1
C 25	0.22-0.29	0.40	0.40-0.70	0.045	0.045	0.40	0.10	0.40	0.63	0.07	25.4
C 30	0.27-0.34	0.40	0.50-0.80	0.045	0.045	0.40	0.10	0.40	0.63	0.07	22.9
C 35	0.32-0.39	0.40	0.50-0.80	0.045	0.045	0.40	0.10	0.40	0.63	0.07	19.7
C 40	0.37-0.44	0.40	0.50-0.80	0.045	0.045	0.40	0.10	0.40	0.63	0.07	17.3
C 45	0.42-0.50	0.40	0.50-0.80	0.045	0.045	0.40	0.10	0.40	0.63	0.08	17.4
C 50	0.47-0.55	0.40	0.60-0.90	0.045	0.045	0.40	0.10	0.40	0.63	0.08	15.7
C 55	0.52-0.60	0.40	0.60-0.90	0.045	0.045	0.40	0.10	0.40	0.63	0.08	14.3
C 60	0.57-0.65	0.40	0.60-0.90	0.045	0.045	0.40	0.10	0.40	0.63	0.08	13.1

As to the sintered materials to be utilized to manufacture powder forged components, the MPIF Standard 35 [10] states: “Nominal carbon content shall be as specified by the purchaser. Unless otherwise agreed upon between the purchaser and manufacturer, the forged product carbon content shall be within ± 0.05 % of the specified carbon content”. Then, the scattering of carbon ranges from 50 %, in the case of 0.20 % C specification, to 27 %, in the case of 0.75 % C specification.

Tab.2. Allowed tolerances on chemistry of special steels, fully dense (casting analysis). EN 10083, Part 1.

Type	Chemical composition, mass %						C ranges	
	C	Mn	Cr	Mo	Ni	V	weight %	relative %
34Cr 4	0.30÷0.37	0.60÷0.90	0.90÷1.20	—	—	—	0.07	20.9
37Cr 4	0.34÷0.41	0.60÷0.90	0.90÷1.20	—	—	—	0.07	18.7
41Cr 4	0.38÷0.45	0.60÷0.90	0.90÷1.20	—	—	—	0.07	16.9
25CrMo4	0.22÷0.29	0.60÷0.90	0.90÷1.20	0.15÷0.30	—	—	0.07	31.1
34CrMo4	0.30÷0.37	0.60÷0.90	0.90÷1.20	0.15÷0.30	—	—	0.07	20.9
42CrMo4	0.38÷0.45	0.60÷0.90	0.90÷1.20	0.15÷0.30	—	—	0.07	16.9
50CrMo4	0.46÷0.54	0.50÷0.80	0.90÷1.20	0.15÷0.30	—	—	0.08	16.0
36CrMoNi4	0.32÷0.40	0.50÷0.80	0.90÷1.20	0.15÷0.30	0.90÷1.20	—	0.08	22.2
34CrNiMo6	0.30÷0.38	0.50÷0.80	1.30÷1.70	0.15÷0.30	1.30÷1.70	—	0.08	23.5
30CrNiMo8	0.26÷0.34	0.30÷0.60	1.80÷2.20	0.30÷0.50	1.80÷2.20	—	0.08	26.7
36NiCrMo16	0.32÷0.40	0.30÷0.60	1.60÷2.00	0.25÷0.45	3.60÷4.10	—	0.08	22.2
51CrV4	0.47÷0.55	0.70÷1.10	0.90÷1.20	—	—	0.10÷0.25	0.08	15.7

Si max. 0.40 %; P max. 0.035 %; S max. 0.035 %

Tab.3. Tolerances on chemical composition of PM steels. AFNOR (ISO) and DIN Standards [6, 7].

Standardization		Chemical composition, mass %							C ranges	
Body	Standard design.	Material code	C %	Cu %	Ni %	Mo %	P %	Mn %	weight %	relative %
AFNOR	ISO 5755-2	P 102x (1)	<0.3	—	—	—	—	—	<0.3	<200
		P 103x (1)	0.3÷0.6	—	—	—	—	—	0.3	67
		P 104x (1)	0.6÷0.9	—	—	—	—	—	0.3	40
		P 202x (1)	<0.3	1÷4	—	—	—	—	<0.3	<200
		P 203x (1)	<0.3	4÷8	—	—	—	—	<0.3	<200
		P 204x (1)	0.3÷0.6	1÷4	—	—	—	—	0.3	67
		P 205x (1)	0.6÷0.9	1÷4	—	—	—	—	0.3	40
		P 206x (1)	0.3÷0.6	4÷8	—	—	—	—	0.3	67
		P 207x (1)	0.6÷0.9	4÷8	—	—	—	—	0.3	40
DIN	30 910 Teil 4	X 00 (2)	<0.3	<1	—	—	—	—	<0.3	<200
		X 01 (2)	0.3÷0.6	<1	—	—	—	—	0.3	67
		X 10 (2)	<0.3	1÷5	—	—	—	—	<0.3	<200
		X 11 (2)	0.4÷1.5	1÷5	—	—	—	—	1.1	116
		X 21 (2)	0.4÷1.5	5÷10	—	—	—	—	1.1	116
		X 30 (2)	<0.3	1÷5	1÷5	<0.8	—	—	<0.3	<200
		X 35 (2)	<0.3	<1	—	—	0.3÷0.6	—	<0.3	<200
		X 36 (2)	<0.3	1÷5	—	—	0.3÷0.6	—	<0.3	<200
		X 39 (2)	0.3÷0.6	1÷3	1÷5	<0.8	—	—	0.3	67
	30 910 Teil 6	F 00 (3)	0.3÷0.5	—	—	—	—	0.3÷0.4	0.2	50
		F 30 (3) (4)	0.3÷0.5	—	0.2÷0.4	0.2÷0.4	—	0.3÷0.4	0.2	50
		F 31 (3)	0.3÷0.5	—	1.8÷2.0	0.5÷0.6	—	0.2÷0.3	0.2	50

AFNOR: Association française de Normalisation, DIN: Deutsche Industrie Normen, ISO: International Standard for Organization.

- (1) x designates the typical relative density: 2 – 75 %; 3 – 80 %; 4 – 85 %; 5 – 90 %; 6 – 94 %.
- (2) X designates the density range: C - $6.4 \div 6.8 \text{ g/cm}^3$; D - $6.8 \div 7.2 \text{ g/cm}^3$; E - $> 7.2 \text{ g/cm}^3$.
- (3) F designates sinter forged materials, with density $> 7.5 \text{ g/cm}^3$.
- (4) Cr range: $0.1 \div 0.25$.

Tab.4. Tolerances on chemical composition of PM steels. Japanese Industrial Standards, JIS Z 2550: 2000 [8].

Material		Chemical composition, by weight						C ranges	
Category	Code	C %	Cu %	Ni %	Mo %	P %	Mn %	weight %	relative %
Iron	P102n(1)	<0.3	—	—	—	—	—	<0.3	<200
C steel	P103n(1)	$0.3 \div 0.6$	—	—	—	—	—	0.3	67
	P104n(1)	$0.6 \div 0.9$	—	—	—	—	—	0.3	40
Cu steel	P202n(1)	<0.3	$1 \div 4$	—	—	—	—	<0.3	<200
	P203n(1)	<0.3	$4 \div 8$	—	—	—	—	<0.3	<200
Cu-C steel	P204n(1)	$0.3 \div 0.6$	$1 \div 4$	—	—	—	—	0.3	67
	P205n(1)	$0.6 \div 0.9$	$1 \div 4$	—	—	—	—	0.3	40
	P206n(1)	$0.3 \div 0.6$	$4 \div 8$	—	—	—	—	0.3	67
	P207n(1)	$0.6 \div 0.9$	$4 \div 8$	—	—	—	—	0.3	40
P steel	P106n(1)	<0.3	—	—	—	$0.2 \div 0.5$	—	<0.3	<200
	P108n(1)	<0.3	—	—	—	$0.5 \div 0.65$	—	<0.3	<200
P-C steel	P107n(1)	<0.3	—	—	—	$0.2 \div 0.5$	—	<0.3	<200
	P109n(1)	<0.3	—	—	—	$0.5 \div 0.65$	—	<0.3	<200
Cu-P steel	P209n(1)	$0.3 \div 0.6$	$1 \div 4$	—	—	$0.2 \div 0.5$	—	0.3	67
	P212n(1)	$0.3 \div 0.6$	$1 \div 4$	—	—	$0.5 \div 0.65$	—	0.3	67
Cu-C-P steel	P210n(1)	$0.3 \div 0.6$	$1 \div 4$	—	—	$0.2 \div 0.5$	—	0.3	67
	P213n(1)	$0.3 \div 0.6$	$1 \div 4$	—	—	$0.5 \div 0.65$	—	0.3	67
Ni steels	P106n(1)	<0.2	<0.8	$1 \div 3$	—	—	—	<0.2	<200
	P108n(1)	<0.2	<0.8	$3 \div 6$	—	—	—	<0.2	<200
Ni-Cu steels	P109n(1)	<0.3	$1 \div 3$	$1 \div 3$	—	—	—	<0.3	<200
	P109n(1)	$0.3 \div 0.6$	$1 \div 3$	$1 \div 3$	—	—	—	0.3	67
	P212n(1)	<0.3	$1 \div 3$	$3 \div 6$	—	—	—	<0.3	<200
	P212n(1)	$0.3 \div 0.6$	$1 \div 3$	$3 \div 6$	—	—	—	0.3	67
Ni-Cu-Mo steels	P307n(1)	<0.3	$1 \div 3$	$1 \div 3$	$0.3 \div 0.7$	—	—	<0.3	<200
	P308n(1)	$0.3 \div 0.6$	$1 \div 3$	$1 \div 3$	$0.3 \div 0.7$	—	—	0.3	67
	P309n(1)	$0.6 \div 0.9$	$1 \div 3$	$1 \div 3$	$0.6 \div 0.7$	—	—	0.3	40
	P310n(1)	$0.3 \div 0.6$	$3 \div 6$	$1 \div 3$	$0.3 \div 0.7$	—	—	0.3	67
Prealloyed Ni-MoMn steel	P311n(1)	$0.4 \div 0.7$	$0.35 \div 0.65$	—	$0.50 \div 0.70$	—	$0.25 \div 0.60$	0.3	55
	P312n(1)	$0.4 \div 0.7$	$1.70 \div 2.00$	—	$0.45 \div 0.65$	—	$0.15 \div 0.60$	0.3	55

- (1) n designates the typical density; range amplitude: 0.4 g/cm^3 . 2 - 5.8 g/cm^3 ; 3 - 6.2 g/cm^3 ; 4 - 6.6 g/cm^3 ; 5 - 7.0 g/cm^3 ; 6 - 7.3 g/cm^3 .

Tab.5. Tolerances on chemical composition of PM steels. MPIF (Metal Powder Industries Federation) Standard 35: Material Standards for PM Structural Parts, 2000 edition. [9].

Material		Chemical composition, by weight						C ranges	
Category	Code	C %	Cu %	Ni %	Mo %	P %	Mn %	weight %	relative %
Iron and Carbon Steel	F-0000	0.0÷0.3	—	—	—	—	—	0.3	200
	F-0005	0.3÷0.6	—	—	—	—	—	0.3	67
	F-0008	0.6÷0.9	—	—	—	—	—	0.3	40
Iron-Copper and Copper Steel	FC-0200	0.0÷0.3	1.5÷3.9	—	—	—	—	0.3	200
	FC-0205	0.3÷0.6	1.5÷3.9	—	—	—	—	0.3	67
	FC-0208	0.6÷0.9	1.5÷3.9	—	—	—	—	0.3	40
	FC-0505	0.3÷0.6	4.0÷6.0	—	—	—	—	0.3	67
	FC-0508	0.6÷0.9	4.0÷6.0	—	—	—	—	0.3	40
	FC-0808	0.6÷0.9	7.0÷9.0	—	—	—	—	0.3	40
	FC-1000	0.0÷0.3	9.5÷10.5	—	—	—	—	0.3	200
Iron-Nickel and Nickel Steel	FN-0200	0.0÷0.3	0.0÷2.5	1.0÷3.0	—	—	—	0.3	200
	FN-0205	0.3÷0.6	0.0÷2.5	1.0÷3.0	—	—	—	0.3	67
	FN-0208	0.6÷0.9	0.0÷2.5	1.0÷3.0	—	—	—	0.3	40
	FN-0405	0.3÷0.6	0.0÷2.0	3.0÷5.5	—	—	—	0.3	67
	FN-0408	0.6÷0.9	0.0÷2.0	3.0÷5.5	—	—	—	0.3	40
Low Alloy Steel	FL-4205	0.4÷0.7	—	0.35÷0.55	0.50÷0.85	—	—	0.3	55
	FL-4405	0.4÷0.7	—	—	0.75÷0.95	—	—	0.3	55
	FL-4605	0.4÷0.7	—	1.70÷2.00	0.40÷1.10	—	—	0.3	55
	FLN-4205	0.4÷0.7	—	1.35÷2.50	0.49÷0.85	—	—	0.3	55
	FLN2-4405	0.4÷0.7	—	1.00÷3.00	0.65÷0.95	—	—	0.3	55
	FLN4-4405	0.4÷0.7	—	3.00÷5.00	0.65÷0.95	—	—	0.3	55
	FLN6-4405	0.4÷0.7	—	5.00÷7.00	0.65÷0.95	—	—	0.3	55
	FLNC-4405	0.4÷0.7	1.0÷3.0	1.00÷3.00	0.65÷0.95	—	—	0.3	55
Sinter Hardened Steel	FLN2-4408	0.6÷0.9	—	1.00÷3.00	0.65÷0.95	—	—	0.3	40
	FLN4-4408	0.6÷0.9	—	3.00÷5.00	0.65÷0.95	—	—	0.3	40
	FLN6-4408	0.6÷0.9	—	5.00÷7.00	0.65÷0.95	—	—	0.3	40
	FLN-4608	0.6÷0.9	—	3.6÷5.0	0.39÷1.10	—	—	0.3	40
	FLC-4608	0.6÷0.9	1.0÷3.0	1.60÷2.00	0.39÷1.10	—	—	0.3	40
	FLC-4908	0.6÷0.9	1.0÷3.0	1.0÷3.0	1.30÷1.70	—	—	0.3	40
	FLNC-4408	0.6÷0.9	1.0÷3.0	1.0÷3.0	0.65÷0.95	—	—	0.3	40
Diffusion Alloyed Steel	FD-0200	0.0÷0.3	1.3÷1.7	1.55÷1.95	0.4÷0.6	—	—	0.3	200
	FD-0205	0.3÷0.6	1.3÷1.7	1.55÷1.95	0.4÷0.6	—	—	0.3	67
	FD-0208	0.6÷0.9	1.3÷1.7	1.55÷1.95	0.4÷0.6	—	—	0.3	40
	FD-0405	0.3÷0.6	1.3÷1.7	3.60÷4.40	0.4÷0.6	—	—	0.3	67
	FD-0408	0.6÷0.9	1.3÷1.7	3.60÷4.40	0.4÷0.6	—	—	0.3	40

A simple comparison between fully dense – or “conventional” – steels and the PM ones shows that the tolerances on carbon content strongly differ. Consequently, it may be interesting to evaluate how much this difference can affect the mechanical properties. To assess in a first approximation, the influence of variations of carbon content on tensile properties of PM steel, it is first necessary to account for the influence of density. To this purpose, the formula $R_s = R_0 \cdot \rho^{3,4}$, proposed by Exner and Pohl [11], may be applied. R_s is the

ultimate tensile strength of a sintered steel having ρ relative density and R_0 is the ultimate tensile strength of the corresponding (as to composition and microstructure) fully dense steel.

Then, after quenching and tempering at 425°C, we should have:

at 6.8 g/cm³ density ($\rho = 0.866$): $R_s = 788.4 \times C \% + 173.8$ MPa,

at 7.2 g/cm³ density ($\rho = 0.917$): $R_s = 967.5 \times C \% + 211.0$ MPa.

If density and carbon content excursions combine in the most unfavourable manner, the possible extreme values are

410.3 MPa at 6.8 g/cm³ density and 0.3 % C,

791.5 MPa at 7.2 g/cm³ density and 0.6 % C,

or, in other terms, the ultimate tensile strength would be 601 ± 32 % MPa.

Analogous calculations could be carried out to evaluate U.T.S. in the normalized state, thus obtaining 421 ± 34 % MPa. These approximate evaluations are clearly penalizing PM steels in any comparison of “precision” with fully dense materials, because the scattering range is more than double. Due to this wide range, any safe design value is adversely affected.

The contribution of the allowed carbon range to scattering of properties is comparable to the contribution of density. These approximate but simple evaluations constitute a threat – or at least a heavy limitation – to any application of new PM parts for sophisticated and exacting applications: to guarantee the minimum property value, a lot of superabundant (and costly) parts will be the rule. This point may be seen as an unpleasant assessment, but it is only a harsh picture of the current situation.

Tab.6. Properties of sintered materials depending on crystal lattice, density, carbon content.

Type of elementary cell	Property depending on	
	Density	Carbon content
Thermal expansion coefficient	Electrical conductivity	Thermal expansion coefficient
Heat capacity	Heat conductivity	Temperature of lattice transformations
Temperature of lattice transformations	Ultimate tensile strength	Temperature of microstructural transformations
Temperature of microstructural transformations	Yield strength	Melting temperature
Creep temperature	Fatigue resistance	“True” hardness (or hardness of the “single grain”)
Melting temperature	Rupture elongation	Electrical conductivity
Boiling temperature	Wear resistance	Heat conductivity
Sublimation temperature	Apparent hardness	Ultimate tensile strength
“True” hardness (or hardness of the “single grain”)	Moduli of elasticity	Yield strength
	Poisson coefficient	Fatigue resistance
	Hardenability	Rupture elongation
	Case hardening depth	Wear resistance
	Induction hardening depth	Apparent hardness
		Hardenability
		Case hardening depth
		Induction hardening depth

As it is known, the presence of other suitable alloy elements, in addition to carbon, strongly enhances the properties of fully dense steels. The ruling parameters on which mechanical properties depend are the typical microstructures which form upon cooling when carbon is present. It should be unquestionable that the same positive effects of additions of carbon plus suitable alloy additions should hold for PM (either porous or non

porous) steels. For not completely dense materials however, as already anticipated, the influence of porosity must be considered. For long time it has been demonstrated that all the properties of porous materials not depending on base-metal features - i.e. on its crystal lattice - are linked to porosity [12,13,14,15]. Then, any survey of properties of PM materials should enable one to distinguish between those depending only on the crystal lattice (of course unaffected by porosity) and those depending on material porosity.

To be complete, it may be interesting to extend the consideration of influencing variables even to the carbon content. The corresponding pattern is presented in Table 6, which clearly demonstrates the substantial effects of carbon content on the highest number of properties of porous steels. Once again, these indications show that a narrow range of carbon content should be seen as a basic requisite to achieve specific and repeatable strength levels even for sintered steels, while reducing chemistry and density redundancies, which unavoidably increase the total production costs.

“UNIT STEPS” OF A SINTERING PROCESS

As everybody knows, even among most PM users, the production processes of PM steels involve the preparation of mixes, containing precise amounts of graphite, followed by sintering under controlled conditions. To fulfill specific requirements, other processes or post-sintering operations may be carried out. The admixing of graphite to iron is necessary to avoid dramatic drops of powder mix compressibility. Figure 1 shows that even low amounts of combined carbon added to iron bring about significant increases of the material yield strength. Other conditions being equal, yield strength may be considered as the main material characteristic on which powder compressibility depends. Furthermore, even if it could be feasible to compact steel powders, i.e. ferrous powders already prealloyed with carbon, the sintering conditions should still be properly set in order to maintain the requested carbon content, as we will see next. By and large, the sintering process can be ideally subdivided into unit stages, according to the scheme of Table 7 [16]. Some single stages overlap each other. A few comments may contribute to a better understanding of a steel sintering process.

1 - The removal of pressing lubricant occurs through different mechanisms. During the heating stage of compacts, when the softening or melting point of the lubricant is reached, a liquid phase is formed. Depending part on geometry and density, some lubricant can percolate across the porosity and drip from the bottom. At a higher temperature the remaining lubricant decomposes, to form heavy hydrocarbons. These heavy hydrocarbons (hexadecane and heptadecane, for instance) are rather unstable and decompose, step by step, in lighter hydrocarbons, up to methane. In certain conditions, some nascent carbon is also present, which reacts with iron to form a stable cementite, harmful in many aspects. Some atmospheres and certain lubricants promote this unwanted reaction, within a critical temperature range. A slow heating between 400 and 600°C worsens the problem.

2 - The heat exchange mechanisms change during the process. Conduction is always negligible, whereas convection should predominate below 800°C and radiation should definitely be the prevailing mechanism above 800°C. These temperature ranges show that atmosphere composition can play a basic role upon heating, and on cooling as well. Useful data on some physical properties of atmosphere constituents will be presented later on.

3 - Chemical reactions can occur among the solid constituents of powder mixes. The oxide layers covering the surface of iron particles can react with carbon, from graphite. The extent of such carbon depletion is a function of a typical powder property, the so-called hydrogen loss. If the chemistry of a certain base powder changes lot by lot, the carbon content after sintering can also present some unwanted scattering, more pronounced at the part's core.

4 - Different chemical reactions can occur among the solid constituents of the powder mix and the surrounding and permeating (inside the porosity net) protective atmosphere. The chemical equilibria indicate the possible evolution and the composition changes, but the extent of any reaction depends on local conditions. The porosity can be the cause of chemical gradients, independent from external driving forces and “apparent” external equilibria.

5 - The diffusion of alloy additions should be preceded by a complete reduction of the oxide layers covering the surfaces of metal particles. If oxide residuals remain, embedded in the microstructure, the mechanical properties are adversely affected. The diffusion extent depends on sintering time and, above all, on processing temperature. According to equilibrium conditions and cooling speed, some reversal of the previous diffusion can occur during the cooling stage that follows sintering.

6 - The microstructures formed on cooling depend on local chemical composition and cooling speed. Upon cooling, the heat transfer from the parts, towards furnace walls and protective atmosphere as well, also depends on the type of gaseous mixture surrounding and permeating the parts' porosity.

Tab.7. “Unit” stages occurring during the sintering of steels.

No.	Unit Stage	Temperature range, °C
1	Lubricant removal, in the liquid state	150÷200
2	Lubricant removal, by gaseous decomposition	300÷600
3	Refining (reduction of iron oxide)	750÷1000
4	Carbon diffusion	900÷1050
5	Diffusion of alloy additions	1050÷1300
6	Carbon pick-up by the atmosphere (in some cases)	1000÷1300
7	Carbon restoration	1050÷800
8	Microstructure formation	950÷600
9	Final cooling, under reducing or “inert” conditions	600÷50

CONTROLLED ATMOSPHERES

Considering only the sintering of carbon-containing steels, the possible atmospheres which depend also on the type of alloy additions, may be:

- endogas from gaseous hydrocarbons (usually methane or propane),
- synthetic endogas (mixtures of methanol and nitrogen),
- pure hydrogen,
- cracked ammonia,
- nitrogen based mixes ($N_2 + H_2$) without carburizing additions,
- nitrogen based mixes ($N_2 + H_2$) with carburizing additions,
- highly diluted endogas,
- vacuum.

Case by case, the chemical composition of any controlled atmosphere depends on a local source of base gas. Just as a reference, some typical values are collected in Tab.8. For a better understanding of the dynamic situations occurring during sintering, the different atmospheres are examined separately.

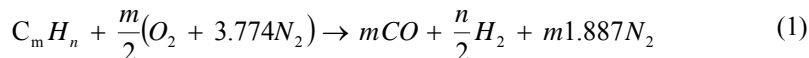
Table.8. Typical compositions of controlled atmospheres.

Type	Chemical composition, %								Dew point °C
	N ₂	H ₂	CO	H ₂ O	CO ₂	O ₂	CH ₄	NH ₃	
1	38.5	40.5	20.1	0.3	0.08	—	0.5	0.0	0
2	41.5	37.5	19.0	1.2	0.3	—	0.4	0.0	15
3	44.7	31.0	23.3	0.5	0.1	—	0.3	0.0	10
4	—	> 99.9	—	0.01	—	—	—	—	- 60
5	> 99.9	—	—	0.01	—	—	—	—	- 60
6	25.0	75.0	—	0.05	—	—	—	< 0.003	- 50
7	90.0	9.9	—	0.01	—	—	—	—	- 60
8	90.0	9.5	—	0.02	—	—	0.5	—	- 55
9	84.5	10.0	5.0	0.1	0.005	< 5 ppm	0.3	—	- 30
10*	—	—	—	—	—	—	—	—	- 80

* “Vacuum”, absolute pressure $0.13 \div 0.15$ Pa, corresponding to $0.98 \div 1.13$ $\mu\text{m Hg}$.

Endogas from gaseous hydrocarbons

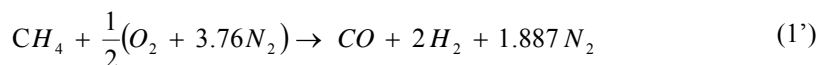
Presumably, Koebel [17,18] and Gurry [19] were among the first scientists to write fundamental papers on controlled atmosphere, either obtained by partial combustion of natural gas and to be used to sinter ferrous base materials, or generated in various ways and formulated to be in equilibrium with a defined carbon content of fully dense steels. Other significant contributions have been given by Durdaller [20], Bocchini [21], Mosca [22, 23], and Beiss [24]. To generate a carbon-containing controlled atmosphere, a light hydrocarbon gas is partially burnt inside a catalytic retort, heated up to $1000 \div 1100^\circ\text{C}$. In the most general case, the simplified reaction between hydrocarbon and air is the following



To obtain only CO and H₂ the “exact” air/gas ratio should be

$$\frac{m}{2}(1 + 3.774) = m2.387$$

In the case of methane the latter reaction becomes



with the “exact” air/gas ratio equal to $(m/2)(1 + 3.774)$, namely 2.387.

Correspondingly, the gaseous composition at the generator exit should ideally be H₂ = 40.9 %, N₂ = 38.6 %, CO = 20.5 %.

For comparison, in the case of complete combustion to CO₂ and H₂O, the stoichiometrical ratio between air and gas should be equal to $(m + n/4)(1 + 3.774)$. Therefore, the ratio $(m/2)/(m + n/4)$ may be seen as a relative measure of the “distance” from complete combustion. For an endogas from methane this ratio is equal to 1/4. According to Koebel [17,18], the reaction (1') is exothermic at a high temperature, but some energy is required to reach the required operating conditions. For this reason, for a long time, the incorrect term “endogas” has been and is still used. At a high temperature, other chemical reactions may occur among the various substances. These are listed in Table 9, with their corresponding equilibrium constants. Chemical equilibrium means that there is no further tendency for the substances concerned to react or, in terms of the theory of reaction rates, that the rates of reaction in the forward and reverse directions are equal. Then, at equilibrium (at a given temperature) the ratio between the concentration of products and

concentration of reactants remains constant. For gaseous substances, assuming an ideal behavior, concentrations are directly proportional to partial pressures. The equilibrium curves are plotted in Figs.2, 3 and 4. For the calculations, the data published in a valuable paper published by Beiss [24] have been utilized. All plots show that in parallel with the simplified reaction (1'), other chemical exchanges occur. In addition, it is possible to observe that the chemical composition of any gaseous mix at the exit of the catalytic retort strongly depends on working temperature and uncontrolled temperature changes. For this reason and to avoid unpredictable changes, the generated atmosphere must be cooled quickly. In the case of too slow of a cooling, soot will form according to reaction (2). The equilibrium curve relevant to reaction (3) shows that some free methane will also remain in the atmosphere. Figure 4 indicates that the oxidizing substances H₂O and CO₂ are always present. While H₂O - at least in principle - could be removed by physical methods, CO₂ will instead remain in the gas entering the sintering furnace. As a consequence, the equilibrium carbon content in the austenite (the only microconstituent into which carbon can diffuse) will be affected. In writing the simplified reaction (1'), a constant air/gas ratio was assumed. If this ratio is <2.387, some free carbon will remain and soot will form inside the generator. Then, the lowest air/gas ratio should be fixed at 2.4. The amount of air can be increased, within certain limits, to modulate the carbon equilibrium during sintering, which is defined by the CO/CO₂ ratio. When the air/gas ratio changes, the chemical composition of the gas at retort exit changes as well. The influence of this feeding ratio on the relative quantities of (partial) combustion products is plotted in Fig.5 - at 1100°C (partial) combustion temperature - mainly based on the data published by Beiss [24]. The quantities of oxidizing substances have been obtained instead by calculations, with some simplifying hypotheses. The log scale, not frequent when plotting compositions, allows reading with enough precision the percentages of "minor" but dangerous constituents, H₂O and CO₂. According to the equilibrium constant of reaction (3), the residual content of methane should be very small, provided that the air/gas ratio is higher than the limit corresponding with soot formation. When the air/gas ratio increases from 2.4 to 3.0 the chemical composition of the atmosphere changes as follows:

- nitrogen increases from 38.9 % to 44.15 %,
- hydrogen decreases from 40.5 % to 31.5 %,
- carbon monoxide decreases from 20.1 % to 16.9 %,
- water increases up to 5.5 %,
- carbon dioxide increases up to 1.6 %.

All the changes follow nearly linear courses.

For a modest change of air/gas ratio (for instance, between 2.4 and 2.6), we can assume that H₂ is always 39.5 % and CO remains at about 19.8 %. Then, within this interval, the ratio between reducing agents is nearly equal to 2.0 and the equilibrium constant of reaction (4) can be expressed as

$$K_4 = 2 \frac{P_{CO_2}}{P_{H_2O}} \quad (5)$$

Tab.9. “Antagonist” or parallel reactions occurring inside an endogas generator (carbon activity assumed to be 1; graphite is formed as equilibrium phase).

Chemical reaction	Equilibrium constant
$2\text{CO} = \text{CO}_2 + \text{C}$ (2)	$K_2 = \frac{P_{\text{CO}_2}}{P_{\text{CO}}^2}$
$2\text{H}_2 + \text{C} = \text{CH}_4$ (3)	$K_3 = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2}$
$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ (4)	$K_4 = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$

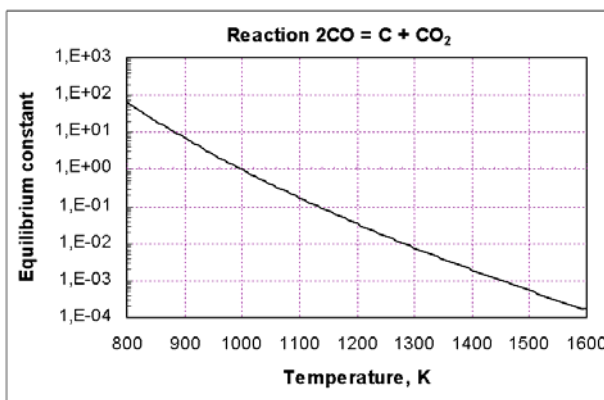


Fig.2. Equilibrium constant for the reaction between carbon monoxide and carbon dioxide.

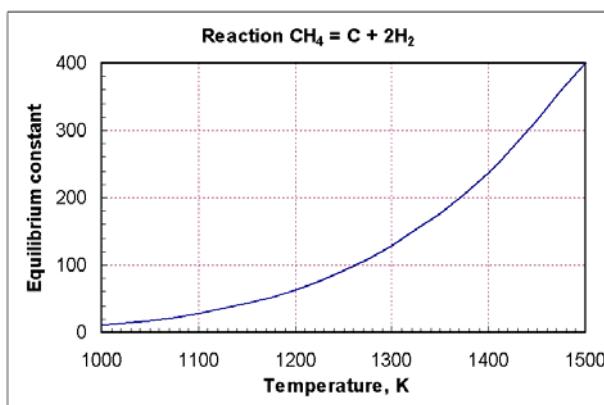


Fig.3. Equilibrium constant for the reaction of methane splitting, to form carbon and hydrogen.

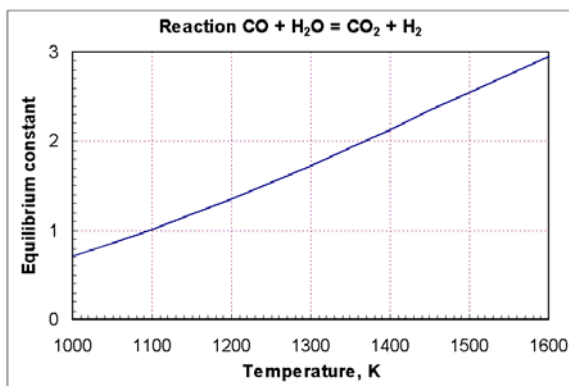


Fig.4. Equilibrium constant for the so-called water-gas reaction.

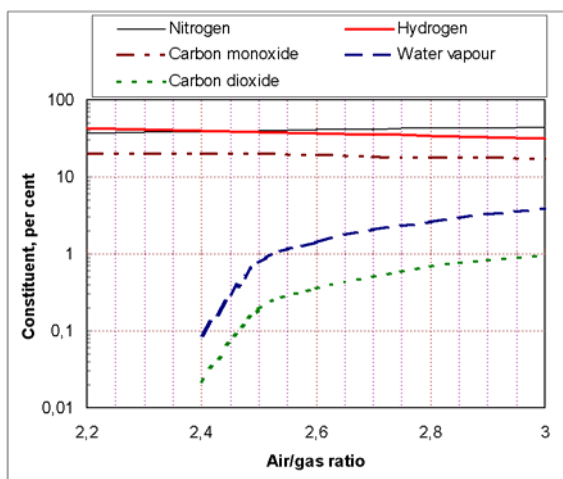


Fig.5. Chemical compositions of (partial) combustion products from methane, at 1100°C. Soot formation below 2.4 ratio (redrawn, from Beiss [24]).

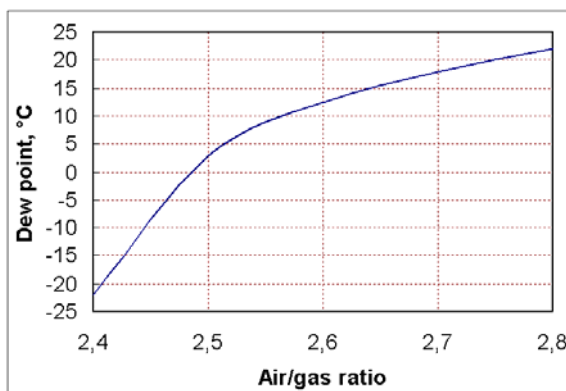


Fig.6. Dew point of endogas atmospheres, from methane, versus air/gas ratio (with negligible methane content).

This result means that at a constant temperature of atmosphere generation, the ratio between H_2O and CO_2 is a constant. Then it should be clear that the possible interactions between atmosphere and sintering (or heat treating) material - at any temperature - could be evaluated measuring either CO_2 or H_2O content. Customarily, the H_2O content is measured by detecting the atmosphere dew point. It may be interesting to utilize the curves of Fig.5 to plot the dew point of endogas from methane versus the air/gas ratio. Assuming that the CH_4 content is negligible, it is possible to combine equilibrium conditions and mass balances, to find the compositions corresponding to different air/gas ratios. The results of calculations have been utilized to plot, in Fig.6, the dew point versus the feeding ratio at the generator. Both Figures 5 and 6 shows that to get a consistent result, a fine "tuning" of the air/gas ratio is required. A similar analysis can be carried out on other types of endogases, based on other light hydrocarbons. It should be stressed that the chemical composition at the exit of the catalytic retort is defined by feeding ratio and operating temperature. The curves of various equilibrium constants show, indeed, that any temperature change brings about significant changes in chemical compositions of controlled atmospheres. Therefore, any endogas, when produced at a given selected temperature, should be cooled as fast as possible to avoid any possible unwanted and uncontrolled change of composition. For the same reason, the atmosphere entering the furnace should be heated as fast as possible, to avoid as well any possible unwanted and uncontrolled alteration.

Pure hydrogen

In this case the chemical composition depends on the gas supplier. With correct process conditions the dew point could be even lower than that indicated in Table 4. Some PM engineers believe that hydrogen is decarburizing. This point is not correct and will be discussed more deeply in an upcoming paragraph.

Pure nitrogen

Also in this case the chemical composition depends on the gas supplier. With correct process conditions the dew point could be even lower than that indicated in Table 4. The nitriding potential - at least when sintering carbon steels - can be neglected.

Cracked ammonia

For many years this atmosphere was the most convenient in many sintering plants. Even today, according to German [25], "dissociated ammonia is a relatively low cost reducing atmosphere to sinter many metallic materials. The dissociation reaction occurs on a heated catalyst (near $1000^\circ C$) to give a pure, low-moisture-content atmosphere. Residual ammonia is typically below 250 ppm, and as long as the moisture content is low the atmosphere is nearly neutral with respect to carbon."

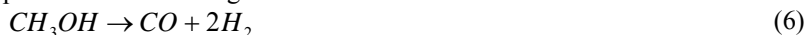
Nitrogen based atmospheres

PM parts makers, depending upon available equipment and material requirements, establish the chemical compositions. Some addition of reducing agents is common. Therefore, in many cases hydrogen is present, in quantities included between 5 and 12 %. A small amount of CH_4 is added when a carburizing action is required.

"Synthetic" endogas

For several years now, some furnace manufacturers have introduced new types of equipment, using a mixture of methanol (or methyl alcohol) and nitrogen as a controlled

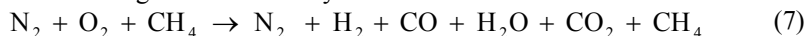
atmosphere. When this mixture is introduced into the sintering zone of the furnace, at a high temperature the following reaction occurs



Because the ratio between CO and H₂ is the same of endogas from CH₄, by adding N₂ it is possible to form an endogas directly inside the furnace. It should be stressed that in this case no atmosphere generator is required. Since methyl alcohol is a liquid at room temperature (its boiling point is 64.7°C), it is possible to calculate that the feeding ratio corresponding to endogas from methane is 1.05 nm³ of nitrogen per litre of liquid methanol. Using higher amounts of nitrogen, "diluted" endogases can be obtained.

Alnat I

This new type of controlled atmosphere is produced by a recently patented Air Liquide process [26,27]. In the first stage, O₂ and CO₂ are selectively removed from compressed air. A nitrogen rich stream, called Floxal, is the primary product. This gaseous mix contains at least 90 % N₂ and other inert gases, O₂, and minor quantities of CO₂ and H₂O, less than 20 ppm each. In a second stage Floxal is made to react with CH₄, to form a strongly diluted endogas. Schematically the reaction is



The reaction is conducted inside a catalytic reactor, heated to a temperature of around 1000 K. The catalyst promotes the selective oxidation of the hydrocarbon. The target is to get as much hydrogen and carbon monoxide as possible and as little H₂O and CO₂ as possible. O₂ from N₂ rich Floxal is consumed by the catalytic reaction and transformed mainly to CO. The name selected by Air Liquide for this type of atmosphere is Alnat I. The residual content of CH₄ in the Alnat I atmosphere can be adjusted between 0 and 1 %, in accordance with the required process parameters.

PHYSICAL PROPERTIES OF THE SINGLE GASES

In most of the papers on controlled atmospheres the constituting gases are considered only as to their chemical behaviour. For a better understanding of sintering results however, their physical properties should also be considered. As a matter of fact, strong viscosity differences, for instance, could bring about some chemical gradients along the open and interconnected porosity. R. German [25] published a table listing some properties of common atmosphere gases, but at temperatures lower than those to select for sintering carbon steel. For this reason, some specific evaluations have been made to estimate the influence of temperature on density, heat capacity, thermal conductivity and viscosity of single gaseous species.

Density

Inside the typical ranges of temperature and pressure used for sintering carbon steels we can admit that the behaviour of the gases involved is correctly described by the laws of the ideal gas. Then the Gay Lussac relation (establishing that at constant pressure the volume is proportional to the absolute temperature) can be applied. Further more, remembering the Avogadro law, the volume occupied by a mole of gas in standard conditions is a constant. The results of these simple calculations have been collected in Table 10, which shows that hydrogen is different from all the remaining gases by an order of magnitude.

Heat capacity

The values of this property at constant pressure (1 bar, 10⁴ N/m²) and different temperatures have been taken from tables published in the Handbook of Chemistry and

Physics [28]. The values relevant to atmosphere gases to be considered in the case of carbon steel sintering are listed in Table 11. It is clear that methane, and especially methanol, notably differ from all other gases.

Thermal conductivity

To find approximate values of such a property, the correspondence law suggested by Perry [29] has been applied. According to this reference it should be

$$\ln k = a \times \ln T + c \quad (8)$$

where k is the thermal conductivity at the absolute temperature T , while a and c are typical constant values for any given gas. In order to find the thermal conductivities at relatively high temperatures, the linear regression analysis has been applied to the data published in [28] for 600 K maximum. For all the gases, the correlation indexes have been always > 0.998 . The results of calculations are listed in Tab.12.

Viscosity

Also in this case, the simple law suggested by Perry [29] has been applied. According to this reference it is

$$\frac{\mu}{\mu_0} = \left(\frac{T}{273} \right)^n \quad (9)$$

where n is a constant depending on the selected gas. The calculated data agree well with the nomograph published by Perry [29]; they are collected in Table 13.

Tab.10. Influence of temperature on densities [kg/m³] of atmosphere gases.

Single Gas	Temperature, K							
	800	900	1000	1100	1200	1300	1400	1500
N ₂	0.427	0.379	0.341	0.310	0.284	0.262	0.244	0.228
H ₂	0.0307	0.0273	0.0245	0.0223	0.0205	0.0189	0.0175	0.0164
CO	0.426	0.379	0.341	0.310	0.285	0.262	0.244	0.227
H ₂ O	0.274	0.244	0.219	0.199	0.183	0.169	0.157	0.146
CO ₂	0.667	0.595	0.536	0.487	0.448	0.412	0.383	0.357
CH ₄	0.244	0.217	0.195	0.177	0.163	0.150	0.139	0.130
NH ₃	0.259	0.230	0.207	0.189	0.173	0.160	0.148	0.138
CH ₃ OH	0.488	0.433	0.390	0.355	0.325	0.300	0.279	0.260

Tab.11. Influence of temperature on heat capacity [J/K mole] of atmosphere gases.

Single gas	Temperature, K							
	800	900	1000	1100	1200	1300	1400	1500
N ₂	31.43	32.09	32.70	33.24	33.72	34.15	34.52	34.84
H ₂	29.62	29.88	30.20	30.51	30.99	31.42	31.86	32.30
CO	31.90	32.57	33.18	33.71	34.17	34.57	34.99	35.21
H ₂ O	38.80	40.08	41.39	42.68	43.93	45.14	46.28	47.36
CO ₂	51.44	53.01	54.03	55.42	56.35	57.14	57.82	58.40
CH ₄	64.08	69.14	73.75	77.92	81.68	85.07	88.11	90.96
NH ₃	51.11	53.77	56.24	58.53	60.64	62.58	64.34	65.94
CH ₃ OH	79.84	85.02	89.60	93.62	97.16	100.28	103.01	105.44

Tab.12. Influence of temperature on thermal conductivity [mW/mK] of atmosphere gases

Single gas	Temperature, K							
	800	900	1000	1100	1200	1300	1400	1500
N ₂	57.3	63.2	69.0	74.7	80.3	85.8	91.3	96.7
H ₂	436	484	531	578	624	669	715	759
CO	58.9	65.2	71.5	77.7	83.8	89.9	95.9	101.8
H ₂ O	67.7	79.1	90.8	193.0	115.5	128.3	141.5	155.0
CO ₂	62.5	73.2	84.3	95.8	107.7	119.9	132.4	145.3
CH ₄	116.3	134.1	152.3	170.9	189.9	209	229	249
NH ₃	101.9	120.9	141.0	161.9	183.7	206	230	254
CH ₃ OH	87.2	106.9	128.4	151.4	176.1	202	230	259

Tab.13. Influence of temperature on viscosity [μ Pa.s] of atmosphere gases.

Single gas	Temperature, K							
	800	900	1000	1100	1200	1300	1400	1500
N ₂	36.8	40.2	43.5	46.8	50.0	53.1	56.2	59.2
H ₂	17.5	19.1	20.4	21.8	23.1	24.4	25.7	27.0
CO	36.0	39.3	42.5	45.6	48.6	51.6	54.5	57.4
H ₂ O	28.5	32.3	36.2	40.0	43.9	47.9	51.8	55.8
CO ₂	36.7	40.9	45.2	49.4	53.6	57.8	61.9	66.1
CH ₄	24.7	27.3	29.8	32.3	34.8	37.2	39.6	41.9
NH ₃	27.7	31.2	34.7	38.2	41.7	45.3	48.8	52.3
CH ₃ OH	26.3	29.4	32.6	35.8	39.0	42.1	45.3	48.4

SINTERING EQUILIBRIA

According to Kaufmann, [30]: "The appropriate atmosphere composition requirements are calculable from thermodynamic data for equilibria between the individual gases involved and carbon in a solution in iron. This type of information is also readily available in the literature as well as from a number of equipment manufacturers in convenient tabulated form. In spite of this, the reduction to the practice of accepted atmosphere control principles has been far from effective. Few, if any, production facilities are capable of maintaining uniform and constant carbon concentrations in iron during normal sintering cycles."

Still according to Kaufmann, [30]: "The use of equilibrium data to calculate compositional requirements for protective atmospheres implicitly assumes that the system in question may be brought to an equilibrium or steady state condition. The steady state differs from a true equilibrium here in that only a partial, or local, equilibrium is established at the metal-vapor interface. In systems with continuously flowing atmosphere and charge the steady state condition is the most frequently achieved. This is done by supplying atmosphere at a rate sufficient to overpower any compositional changes that might occur by reaction of the atmosphere with metal surfaces. It is readily obvious that this situation is not possible with porous metal materials, since the surface extends well into the interior volume and continuous rapid replenishment of atmosphere in contact with these inner surfaces is physically impossible under normal furnace conditions. It is not surprising, therefore, that most of the previous work on atmosphere control has been confined to the matching of

atmosphere compositions, specifically carbon potential, to metal compositions in an attempt to achieve equilibrium conditions”.

The statements made by Kaufmann go back to more than 30 years ago, but they are still completely valid, at least as far as the possibility to reach equilibrium conditions are concerned. As a matter of fact, it should be clear that the carbon potential of the atmosphere can be regulated at best only in the furnace regions nearest to the outer surfaces of the solid material. In addition, any minor change of local temperatures can affect equilibrium ratios. The situation inside the parts is totally different. Indeed, in these regions equilibria can be established only between local carbon and local oxygen or residual water vapor. The effect of the atmosphere inside the parts can be important at relatively low densities. At least qualitatively, the interactions between atmosphere constituents and different chemical compounds inside the parts tend to decrease when porosity decreases. For this reason, the ideal stages of Table 3 should be considered almost completely valid only for the “skin” of PM parts. What really happens at the core strictly depends on pore structure, part volume and part size. For instance, it should be not surprising that high density and large compacts could be badly sintered at the core. This point should be carefully evaluated, for example, when selecting parts’ geometries to be obtained by warm compaction. For a better understanding of actual sintering conditions, certainly different from the classical equilibrium concept, it may be useful to add some basic information on gas-solid reactions, and then discuss separately the different possible atmospheres.

REACTIONS BETWEEN CARBON-CONTAINING GASES AND IRON (AUSTENITE)

According to Krauss [31], “Carbon is introduced into the surface of steel by gas-metal reactions between the various components of an atmosphere gas mixture and the solid solution austenite. Following Harvey [32], reaction (2) is one of the most important carburizing reactions; C is carbon introduced into the austenite. At equilibrium, a carbon ratio of CO₂ and CO has a certain carbon potential or maintains a certain level of carbon in the austenite. At any temperature, the relationship between the gaseous components and the carbon in solution of the austenite is given by the equilibrium constant K, which for reaction (2) may be written as

$$K'_2 = \frac{P_{CO}^2}{a_C \cdot P_{CO_2}} \quad (10)$$

where P_{CO} and P_{CO_2} are the partial pressures of CO and CO₂, respectively, and a_C is the activity of carbon.

The activity of carbon is related to the weight percent of carbon in the austenite by the activity coefficient of carbon, f_c , by the following equation

$$a_C = f_c \text{ wt.\% C} \quad (11)$$

K is a function of temperature, and for the reaction (2) it is

$$\log K = \frac{-8918}{T} + 9.1148 \quad (12)$$

where T is the absolute temperature in degrees Kelvin. The partial pressures of CO and CO₂ required to maintain a given surface austenite carbon content are given by combining Eq. (10) and Eq. (11) as follows:

$$\text{wt.\% C} = \frac{1}{K \cdot f_c} \frac{P_{CO}^2}{P_{CO_2}} \quad (13)$$

If the CO content of an atmosphere exceeds the partial pressure required to maintain a given carbon content, the reaction represented in equation (2), as written, will go to the right and carburizing will occur until a new equilibrium is reached. At the other end, if the CO₂ partial pressure is too high relative to the CO content, the reaction in (2) will go the left and decarburization will occur”.

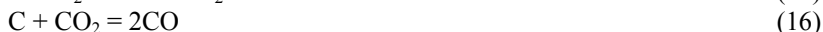
It may be useful to add that the activity of an element dissolved into a solution is given by the ratio between the vapour pressure of the element in solution and the vapor pressure of the pure element in its standard state. In other words, an element being in a non-saturated (solid) solution has a lower activity than the pure element in its standard state at the same temperature. For the pure element in its standard state the activity is 1. Of course, in the case of carbon, graphite can be assumed as a standard state (see, for instance, Kubaschewski et al. [33]). As a rule, when an element is dissolved into a solution, its activity differs from the unity.

INTERACTIONS BETWEEN ATMOSPHERE CONSTITUENTS AND FERROUS MATERIALS UPON SINTERING

The different atmospheres that can be used when sintering PM steels are examined separately.

Endogas from gaseous hydrocarbons

Both hydrogen and carbon monoxide are reducing, but the latter can be more or less strongly carburizing. Just as an example, let us evaluate the H₂ amount required to remove the oxygen content of a typical ferrous powder. In the case of a 100 kg/hour furnace, if the H₂ loss of the base powder is 0.15 %, the quantity of O₂ to be removed in one hour is 0.15 kg. This quantity corresponds to 0.00469 kmoles, requiring 0.00938 kmoles of hydrogen to form 0.00938 kmoles of water vapor. Then the net amount of hydrogen is 0.00938 x 22.414 = 0.21 nm³/hour. Since hydrogen must also permeate the porous material to reach the core of the part, its actual quantity must be definitely higher. The degree of H₂ utilization may be even 10 % or less. Therefore, the hydrogen flow-rate should be at least 2 nm³/hour. If a lower quantity is used, some problems can occur, especially on high density PM parts. Definitely more complicated is the situation as far as the carbon equilibrium is concerned. To this respect, it has already been observed that a given quantity of carbon monoxide can be carburizing or decarburizing, depending on temperature and the required final carbon content or graphite addition. Of course CO₂ and H₂O are decarburizing, while CH₄ is carburizing. The “instant” equilibrium is ruled by the reactions



Following the system used by Beiss [24], the parentheses around C indicate that, in this case, carbon is present as an alloying element dissolved in homogeneous austenite and not as a pure substance in its standard state. The equilibrium constants corresponding to the latter reactions, respectively, are:

$$K_{10} = \frac{p_{CO}^2}{p_{O_2}} \frac{1}{a_c} \quad K_{11} = \frac{p_{CO} p_{H_2}}{p_{H_2O}} \frac{1}{a_c} \quad K_{12} = \frac{p_{CO}^2}{p_{CO_2}} \frac{1}{a_c}$$

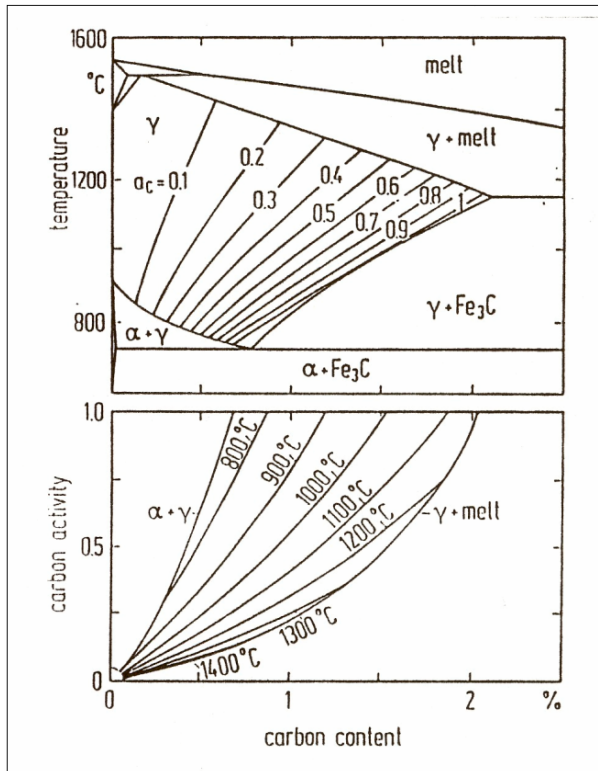


Fig.7. Influence of carbon and temperature on the activity of carbon into unalloyed austenite (from Beiss [24]).

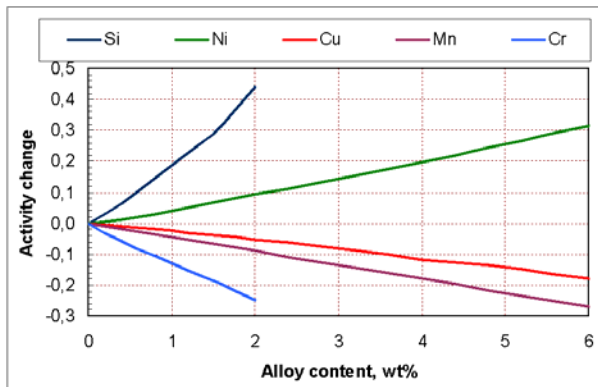


Fig.8. Changes of carbon activity due to the presence of alloy elements evenly distributed in austenite.

As a consequence, it is necessary to consider the relations between temperature, carbon concentration, and alloy additions that could be present in the material. Figure 7, reprinted from Beiss [24], show the changes of carbon activity depending on temperature and steel composition. Figure 8, redrawn on the basis of a more complete one published by

Mosca [22], indicates the changes of carbon activity deriving from the presence of some alloy additions evenly distributed into the ferrous matrix. From the figure we can observe that some alloy elements, for instance Si and Ni, increase the a_c value, whereas other alloy additions like Cu, Mn and Cr, decrease the carbon activity. An increase of a_c means that the C % at equilibrium is reduced if compared with pure carbon. In other words, the presence of such an element as Si or Ni in a solid solution increases a_c , at an identical carbon content, and hence in the terminal solid solubility of C in equilibrium with graphite, it decreases. This means that the presence of Ni or Si brings about a decrease of the carbon content of saturated austenite, and in the pearlite as well. For this reason, the addition of more than 0.7 % carbon to nickel containing PM steels should be avoided, to prevent any possible formation of brittle carbides at the grain borders. At this point it is possible to present the different equilibrium conditions that occur when sintering carbon steels under an endogas atmosphere. Various diagrams, at different times, have been published in literature. They should still be valid, but more recently precise indications have been given by Beiss [24]. The three possible carburizing or decarburizing situations are plotted in Figs.9, 10 and 11. These diagrams enable us to understand why the use of endogas during the sintering of carbon steels requires properly equipped furnaces. For instance, if the atmospheric behaviour is controlled by measuring the CO_2 content, any given gas composition that we can suppose nearly constant above 850°C is given by a point on the x-axis of the corresponding plot. The heating part of the sintering cycle is represented by a downward vertical line on Fig.9, which indicates that the carbon potential of the atmosphere continuously decreases during heating. The so-called carbon potential is the carbon content (in wt. %) of austenite in equilibrium with a given carbon containing atmosphere. Similar indications can be drawn from Figs.10 and 11, depending on the gas constituent that is utilized to control (or "tune-up") the atmospheric properties. Therefore, for carbon steels and endogas atmosphere it is unavoidable that, in the last period of heating before sintering, and during soaking at a maximum temperature as well, a continuous carbon decrement usually occurs. In other words, at a high temperature, and under an endogas atmosphere, a continuous loss of carbon occurs: it is a "normal change" based on thermodynamics. The carbon loss occurs on the surface zones, including some open and interconnected porosity. The idea of increasing the carbon potential at the sintering temperature by changing gas composition is unpractical, and further more, will bring about a too high carbon potential at lower temperatures, with negative effects such as soothing and an uncontrolled cementite net which propagates from the outer surfaces of the parts. The only viable solution when using endogas to sinter carbon steels is to accept a carbon drop at a high temperature, and to compensate for this drop by a soaking time inside a favorable environment at a suitably lower temperature. In the Mid – Sixties this modified sintering process, which included a carbon restoration stage, had been introduced in some advanced PM companies both in North America and in Europe. Kaufmann described this correct approach [30] in a paper that can be considered a milestone in the progress of the sintering process of carbon steel. The carbon restoration zone can be even slightly shorter than the sintering one, due to changes in the physical properties of atmosphere gases during cooling. By using correct equipment and any suitable system for controlling the carbon potential, it is possible to maintain well-defined ranges of combined carbon after sintering. Unfortunately, some manufacturers of furnaces still seem either to neglect or at least underrate this fundamental point when designing PM equipment, even to be used for highly-demanding new processes such as sinter hardening.

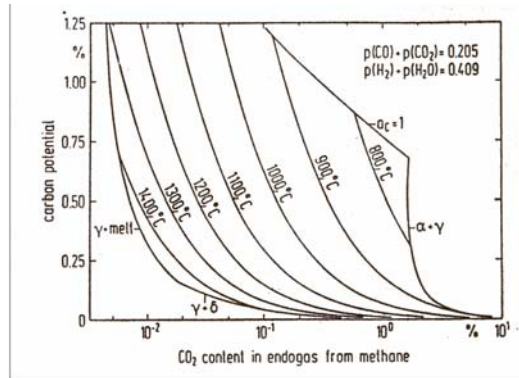


Fig.9. Influence of CO₂ content and temperature on carbon potential of endogas from methane.

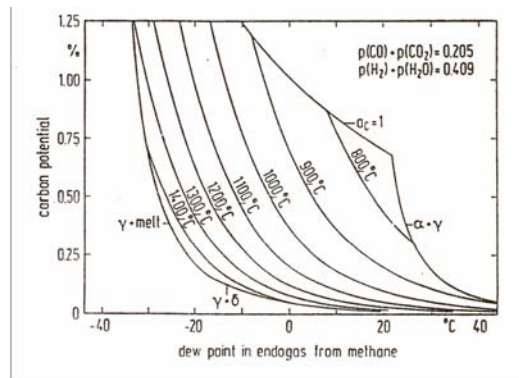
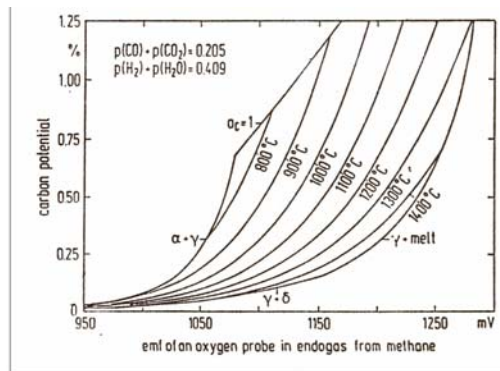


Fig.10. Influence of dew point and temperature on carbon potential of endogas from methane.

Since somebody could object to the previous evaluation, observing that any industrial sintering process is typically a non-equilibrium one (due to the short times usually implied), it may be interesting to try some kinetics consideration. To this purpose, it is necessary to apply of a physical law, known for more than 60 years, which describes the “speed” of carburizing processes. F. E. Harris [34] developed a formula for the effect of time and temperature on case depth:



Fi.11. Influence of O₂ content and temperature on carbon potential of endogas from methane.

$$d = 660 \cdot e^{-8287/T} \cdot \sqrt{t} \quad (17)$$

where: d is case depth, mm
 t is time at temperature, hours,
 T is the absolute temperature, K.

As a rule, the Harris formula (17) is utilized to predict case depth obtained below 965°C, but for times longer than one hour. In our case, on the contrary, the same formula is useful to predict case depth obtained in short times, but in a wide range of temperatures, indicatively from 800 to 1100°C. Figure 12 shows the results of calculations made by applying equation (17) to rather short times, up to half hour. The slope changes – due to the initial stages that have been considered – are hard to detect. The typical parabolic course, (case depth proportional to square root of time) becomes more evident for longer carburizing times. It should be observed that Fig.12 characterizes the process of carbon enrichment occurring when treating fully dense steel. For our purpose, it is necessary to consider the influence of porosity on carbon diffusivity. This subject was investigated by Gallo et al [35], who demonstrated that the apparent diffusion coefficient depends on porosity according to a log law, such as:

$$D \cdot \rho^b = A \quad (18)$$

where:

D is the apparent diffusion coefficient of carbon,
 ρ is the relative density of sintered ferrous material,
 b is a constant, depending on process conditions,
 A is a constant, depending on process conditions.

By means of probes of various geometry, and recording the weight increase during carburizing processes carried out in different conditions, Gallo et al [35] were able to find the relative Harris coefficient, i.e. the influence of material density on the Harris' constant. Figure 13 is based on those results; it shows that the case depth of sintered steel at 7.0 g/cm³ density could be nearly 3 times larger than that observed – under equal process conditions – on fully dense steel.

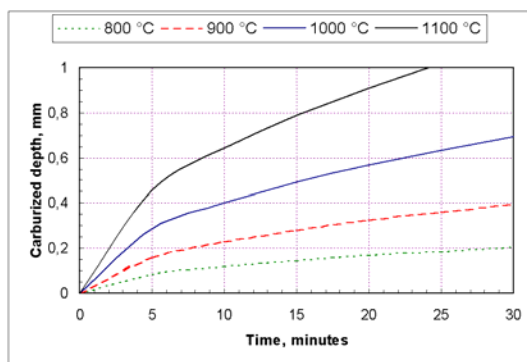


Fig.12. Case depth, evaluated by Harris' formula, for short "carburizing" times; fully dense steel.

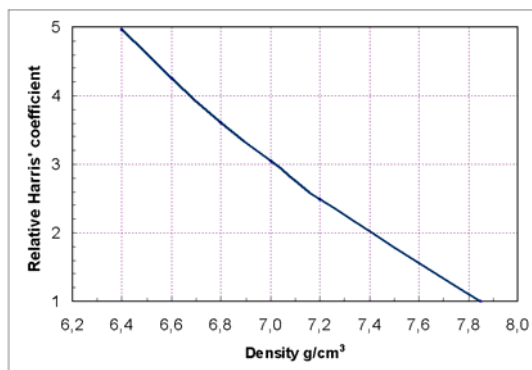
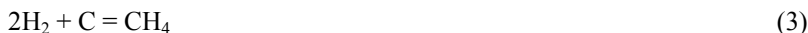


Fig.13. Influence of material' density on case depth: relative Harris coefficient (from [35]).

Decarburizing, even if it is the opposite of carburizing – at least from a physical standpoint – cannot be described in an oversimplified approach by the Harris law preceded by a minus sign. However, at least as to the relative speed, we can admit a similar behavior. Therefore, the de-carburized depth of a PM steel, at 7.0 g/cm³ density, should be nearly three times thicker than that of fully dense steel, treated under the same conditions.

Pure hydrogen

As previously stated, some PM engineers believe that hydrogen is decarburizing. If hydrogen is not polluted by humidity, decarburization occurs through the reaction of methane formation



for which the equilibrium constant is

$$K'_3 = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} \frac{1}{a_c} \quad (3')$$

Figure 3, corresponding to the opposite reaction, enables us to evaluate the possible carbon loss due to this reaction. Let us suppose that the average furnace output is 100 kg/hour, while the atmosphere flow-rate, i.e. pure H₂, is 40 nm³/hour. If the carbon activity is 0.2 (which corresponds roughly to 0.7 % combined carbon) at 1400 K, the equilibrium partial pressure of CH₄ is 0.00083. Then, if the furnace feeding is considered, the amount of CH₄ is 0.0333 nm³/hour, corresponding to 0.00148 kmoles/hour. This quantity can be formed by taking away 0.0178 kg of carbon from the powdered material. Since the amount of carbon entering is 0.7 kg/hour, the calculated carbon decrement reduces the final content to 0.682. Indeed, this simple calculation shows that H₂ is decarburizing, but the carbon loss may be considered negligible even for demanding applications. Further, it seems that the reaction speed is rather low, below 1100÷1200 K.

Then, as to decarburizing, definitely more important is the carbon loss due to the reaction with the oxygen combined with the base metal. Both H₂ and C can react with oxygen, usually indicated as a H₂ loss. The breakdown between reducing agents depends on part geometry, density, temperature gradient, atmosphere flow-rate, gas circulation pattern, and temperature profile. To try to be simple, we can assume that the atmosphere removes half the total O₂, while the remaining amount is removed by carbon from the added graphite. Under this simplifying hypothesis, the “apparent” carbon loss due to H₂ can be evaluated. Let us suppose again that the average furnace output is 100 kg/hour, while the H₂

loss of the base powder is 0.15 %. The oxygen combined with H_2 will be 0.075 kg/hour, which corresponds to 0.00234 kmol/hour. The net amount of H_2 is then 0.00468 kmol/hour, corresponding to 0.105 nm^3 /hour.

Only a fraction of hydrogen entering the furnace reacts with the oxygen inside the parts. As previously stated, at best the "efficiency" of this reaction will attain 10%, so that we can guess that at least 1 nm^3 /hour of H_2 is required. The remaining oxygen will react with carbon, thus lowering its final content. Under the same hypothesis, the carbon decrease due to the powder reduction will be $(12/16) \times 0.075$ kg/hour, namely 0.056 kg/hour. These simple – and approximate – calculations show that the quantity of carbon after sintering – other conditions being equal – will be $0.7 - 0.056 = 0.644$ %. This carbon difference is nearly three times higher than that corresponding to methane formation. If the amount of O_2 removed by H_2 from the powder is less than the estimated value, the carbon loss during sintering increases. For the above reasons, it does not seem correct to consider hydrogen as a "dangerous" decarburizing agent. Of course, if H_2 is not dry enough, a significant carbon decrease comes out from the polluting H_2O . When the dew point of H_2 is known, the relevant calculations can be made as well.

Pure nitrogen

If we neglect any nitriding effect, dry nitrogen is neutral when sintering carbon steels. Nevertheless, a significant carbon decrease will be observed because the added carbon removes the oxygen bonded to iron powder. Considering the same hypothesis as above, this decrease can reach 0.11 %. If N_2 is not dry enough, an additional carbon decrease is originated by H_2O . When the dew point of N_2 is known, the relevant calculations can also be made.

Cracked ammonia

For the gaseous mix obtained by dissociating ammonia the previous considerations can be applied. Also in this case, the dew point plays a basic role.

Nitrogen based atmospheres

When the chemical compositions are known, the interactions between gas constituents and solid materials during sintering may be spotted by adopting the criteria already presented.

The need to add carburizing substances to counteract the trend towards decarburization is frequently a consequence of poor furnace maintenance, which causes air leakage or an uncontrolled pattern of atmosphere circulation inside the furnace itself. If the addition of CH_4 or CO is made to set the correct equilibrium situation for achieving specific carbon content, a precise metering is a necessary but not a sufficient condition. The carburizing effect due to CH_4 increases as the temperature increases. Durdaller [20] published a diagram that shows the changes of equilibrium conditions at different temperatures under a protective atmosphere containing only CH_4 and H_2 . Figure 14 is based on [20], even though the ranges of temperature and CH_4 additions are limited to the possible sintering situations. The slopes of equilibrium lines show that the precise control of carbon potential by methane additions is a very hard task. Furthermore, in the case of N_2 -based atmospheres, CH_4 addition should be decreased with respect to Durdaller's data, since the controlling factor is the ratio $(H_2)^2/CH_4$. Therefore, if H_2 is 10 %, the corresponding additions of CH_4 dramatically decrease. Even if a precise control of very small gaseous flow-rates at least in principle may be possible, the uniform distribution in the "carrier gas" is practically unattainable. In order to get a good mixing, a turbulent gas flow is required.

At the usual speed of the atmosphere inside the furnaces, a mixed flow pattern is a rather common situation, with a possible layering of different substances. In addition, the strong influence of temperature on the carburizing potential of a given CH_4/H_2 ratio must be stressed. Consistent results could be achieved only through a furnace chamber properly maintained at constant temperature. This chamber, designed for a precise “carbon adjustment”, should be placed between the sintering and the controlled cooling section. If a fraction of the atmosphere produced in order to operate inside the carbon control chamber enters the sintering zone, some over-carburizing occurs. The appearance of cementite nets is then probable, especially on the part edges. The penetration of this cementite net depends on time, temperature, and partly density. For all the above reasons, a high quality sintering process can rely on CH_4 additions in case of highly sophisticated equipment only. Where this system is adopted and it seems to work, in the simplest cases, the furnace tightness and the constancy of carbon content at different production times and on different parts should be checked. In some cases, when the risk of air leakages can be excluded, a nitrogen-rich atmosphere with controlled hydrogen additions (as to flow-rates and inlet positions) may enable one to carry out a so-called “neutral” sintering of carbon steels.

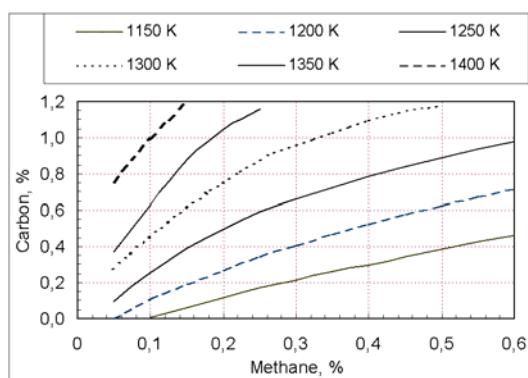


Fig. 14. Influence of methane additions on carbon potential, at different temperatures, of a “pure” hydrogen atmosphere. $\text{CH}_4 + \text{H}_2 = 100\%$.

Alnat I

This new type of atmosphere can be seen as a strongly diluted endogas, with low dew point. Therefore, the continuously changing conditions during heating - which are peculiar of any endogas - have reduced effects, if any. The H_2 content is high enough to offset - at least partially - the carbon decrease due to the oxygen content of the powder. The experience should confirm that, when using consistent raw powders, the carbon decrease upon sintering remains within narrow ranges. Low quality powders, characterized by some (not negligible) scattering in H_2 -loss, will bring about problems in the consistency of carbon content after sintering. As already observed, the experience will give useful indications as to the effects of temperature jump between that of Alnat I generation and the sintering one. The heating from 700°C to 1120°C or more causes an increase of the ratio CO/CO_2 at equilibrium, and then - at least in principle - it should clean and improve the atmosphere effectiveness. If any, the decarburizing effects depending on the possible reaction between CO_2 and C, to form 2CO , should be trifling due to the very small amount of CO_2 . The availability of practical results, based on reliable experiments, possibly confirmed on different equipment, will be useful for a better assessing of this type of atmosphere. At

present, it seems that the applications of Alnat I are still rather limited to some special conditions.

PHYSICAL EFFECTS OF ATMOSPHERE GASES

During sintering the single constituents of controlled atmospheres exert also physical effects: heat transfers and flow inside the porosity, against the counter-flow of the gaseous species originated by chemical reactions, or previously absorbed and then released by desorption on heating. Other conditions being equal, the heating or cooling capacities can be considered proportional to the heat capacities. Table 11 shows that N₂, H₂ and CO are quite similar, whereas CO₂, NH₃, CH₄ and CH₃OH bring about the largest heat exchanges. This point should be considered when adding CH₄ or using CH₃OH to form a controlled atmosphere inside the furnace. Also, in respect to thermal conductivities, heat exchanges can be considered proportional. Table 8 shows that H₂ is more effective than any other atmosphere constituent.

The penetration of gaseous species inside the open porosity should be linked to temperature and flow pattern. Such flow patterns depend on surface roughness of pore channels and on the Reynolds number, i.e. on the dimensionless ratio

$$\text{Re} = \frac{Lv\rho}{\mu} \quad (19)$$

where: Re is the Reynolds' number,
L is a length defining the geometry of the flow system,
v is the fluid speed,
ρ is the fluid density,
μ is the absolute viscosity of the fluid.

According to (19), the ratio between density and viscosity can be assumed as a measure of the resistance to gas penetration inside the pores for any gas and at any temperature. The data collected in Tables 10 and 13 put in evidence that H₂ is at least five times different from the other gases. The availability of specific experimental data will be useful for improving the possibility of a precise control of sintering processes.

SINTERING EQUIPMENT AND PROCESSING CONDITIONS

Some comments on equipment need to be added. When selecting a furnace to be used for sintering carbon steel, changes of atmosphere composition due to thermal profiles of equipment and gas-solid interactions should be adequately considered. Endogas, when used in the simplest equipment is typically decarburizing at high temperature, while carburizing or neutral at 800÷900°C. Not rarely, (as implicitly observed by Kaufmann 30 years ago) this effect dramatically lowers strength and hardness of PM steels. To compensate for the typical high temperature decarburization when using endogas, a suitable carbon restoration zone is compulsory. The length of this chamber could be evaluated by calculations, considering diffusion kinetics and physical properties of different gaseous substances. Positive experiences have been made with the length of this carbon restoration zone at least equal to half the length of the sintering zone. (Obviously, this additional chamber is not required in the case of no-carbon atmospheres). Another basic point is the temperature difference between endogas generation and sintering conditions. The most common solutions include an external generator of atmosphere. It operates at about 1100°C and the atmosphere at the exit is rapidly cooled, to avoid any possible uncontrollable change of its chemical composition. The "cold" endogas is then introduced into the furnace, where it is heated up to the sintering temperature. The heating rate depends on many

factors, so that any complete knowledge of the local atmosphere composition inside a typical sintering furnace, variously loaded, is still lacking. For some years, some furnace manufacturers proposed new concepts of equipment, where the retort to generate endogas is placed just above the sintering chamber and operates at the same temperature. Then, any possible change of chemical composition of the atmosphere due to temperature changes is definitely prevented, at least at the sintering temperature. It seems that one company manufacturing this new type of furnace claims that no carbon restoration zone is required, while carbon potential can be controlled with precision inside the sintering chamber. Due to the high temperature, no soot formation can occur. The latter point is unexceptionable, but some release of carbon on cooling from the atmosphere to the sintered material can always occur. A very fast cooling is needed, from the sintering temperature to about 850°C, to avoid this alteration. The rapid cooling prevents over-carburizing of the material, but it is viable only if the amount of heat to be taken away from the parts is limited: unit mass and extension of external surface of the parts should be in a favorable ratio. Heavy and massy components cool not so quickly, to avoid some carbon enrichment. On this basis the new furnace type appears suitable to the correct sintering of carbon steels if unit weight of the compacts and loading rate are kept below certain limit values. Furthermore, if the carbon potential is at a high temperature, the atmosphere tends to release soot upon cooling. This soot will be formed at the furnace regions where local conditions correspond to a relatively high ratio of CO₂/CO. For a better understanding of these considerations, and assuming that the carbon potential is controlled through an oxygen probe, let us refer to Fig.11. If the combined carbon after sintering at 1120°C (and cooling) must be 0.7 %, the emf of the oxygen probe should be 1184 mV. A vertical line passing on this point, drawn in Fig.11, shows that the carbon potential increases upon cooling, exceeding 1.25 % before crossing the border of the austenite region. Consequently, after crossing this border, a lot of carbide will form or some “unstable” austenite will survive, and the resulting material will be brittle, hard to machine, unsuitable for many applications. The situation is less unfavorable if the part to be sintered at 1120°C must have 0.20 % combined carbon. On this assumption, the emf of the oxygen probe should be 1100 mV. A vertical line passing on this point, drawn in Fig.11, shows again that the carbon potential increases significantly upon cooling, to reach about 0.8 % before crossing the border of the austenite region. Then, no carbide develops after crossing this border and the resulting material will be valid, (remembering the wide tolerance on carbon content required by existing standards), easy to machine and suitable for many applications. From a functional standpoint, the carbon gradient which develops upon cooling may also improve surface properties, even for subsequent heat treatments. However, not negligible carbon excursions appear unavoidable, and the carbon range will be related to part size and surface/volume ratio, because the cooling speed from 1120°C (or 1150°C) to about 800°C depends on environment, atmosphere flow-rate and composition, part mass, material density, and heat exchange surfaces.

In conclusion, if all previous points are properly considered, also the sintering furnaces with an incorporated endogas generator should include a carbon restoration zone. A possible alternative, to be confirmed by systematic experiments, and applicable only to furnaces where the atmosphere generator is located inside the sintering chamber, is the introduction of a fast cooling section, just immediately after the sintering chamber where the load temperature drops very quickly, to about 800°C. In this way, in principle, neither chemical nor microstructural changes could occur, and the carbon equilibrium reached at sintering temperature should be maintained. Presumably, some equipment producer might disprove this position, but all indications based on thermodynamics should be unquestionable.

Furthermore, no experimental results on the matter indicating that chemical changes due to temperature gradients are trifling have been published yet.

For any equipment, it is always necessary to remember that the lubricant removal should be slow below 300°C and as fast as possible between 400 and 600°C, or even high. This need for different heating speeds before reaching 600°C seems to have been neglected by several equipment manufacturers. The problems due to incorrect lubricant removal are higher in the case of endogas, due to the negative effect of CO/CO₂ equilibrium versus temperature. Independently from the atmosphere, a furnace suitable to the correct sintering of carbon steels should be equipped with a controlled cooling section. When this facility is available, the optimum microstructure required by any given application can be obtained. However, the mass of the part may hinder the formation of very fine structures. Then, in the case of large and massy parts, a high alloying content is required to get the fine structures and the strength properties that are typical of less alloyed materials on small parts. Finally, whatever atmosphere and equipment is available, constant and reproducible results can be achieved only if the raw material chemistry, with special attention to H₂-loss of ferrous powders, exhibits minor scattering, lot by lot, and inside the same lot.

REQUIREMENTS ON FERROUS POWDERS

For the proper sintering of carbon steels, the control of atmosphere is a necessary but not sufficient condition. Even optimum equipment and a strict and accurate system of gas control may be thwarted when using raw materials with inconstant properties.

The raw materials to be used to manufacture carbon steels can be subdivided in typical families:

- a) plain iron,
- b) iron base, completely alloyed,
- c) iron base, diffusion bonded,
- d) iron base, with some elements completely prealloyed and some other diffusion-bonded.

In general, if the H₂-loss is high (> 0.2 %), to compensate the carbon drop due to local reactions of material reduction, high graphite additions are needed. Graphite contributes to increase densification levels, but unfortunately decreases green density and green strength. If the scattering on H₂-loss is not negligible, a corresponding scattering on combined carbon content may occur, more or less independently from the atmosphere (especially at the core of heavy and high density parts) with adverse effects on the consistency of mechanical properties and response to some heat treatments.

At equal density and sieve analysis, the particle shape influences the porosity pattern after compaction and sintering. Then, even at equal chemistry, powders of different origin can exhibit different interactions with carbon and atmosphere.

Diffusion-bonded powders, if properly sintered, combine different microstructures, with good influence on fatigue performance. Constant carbon content and a suitable cooling speed after sintering are needed to reach optimum properties. At equal chemistry, density and sintering conditions, the particle shape and bulkiness influence the extent of diffusion of alloying elements. Then diffusion-bonded powders of equal composition, but produced by different processes, are neither equal nor equivalent as far as properties achieved on the corresponding carbon steels. A controlled microstructural unevenness is impossible when using prealloyed powders, but a suitable cooling speed to get possible “optimum” results is still necessary. When using prealloyed powders, requirements on sintering atmospheres may depend more on specific alloying than on carbon control. Endogas and methanol may be unsuitable for the correct sintering of Cr or Mn steels, because some oxide residuals will survive sintering. Some most recent high-property powders have been formulated to reach “treated properties” without the

additional treatments. Due to very high material hardenability, moderately high cooling rates from about 850°C are suitable to originate hard structures directly inside the sintering furnaces, while the last portion of the cooling stage can promote some helpful stress relieving.

If the strong influence of carbon content is properly considered, it should be clear that the tolerances on carbon content should be more narrow than the typical ranges of less sophisticated PM materials. Some experimental results on the influence of the mass (or volume) of the parts on the sintered properties, obtained when combining typical equipment and high-property powders [36,37], indicate that sinterhardened materials may be reliably manufactured only through a careful technical approach.

Furthermore, since the risk of brittleness is a complicated function of part density and alloying content, high compaction (or repressing) densities seem to be compulsory when using powders for sinterhardening.

SOME COMMENTS ON SINTERING EQUIPMENT

For many years now, the evolution of PM technology has been astonishing. New powders have been introduced, suitable to enhance strength and other properties of sintered materials. New tool materials are available, so that higher compaction pressures can be used and higher green densities can be attained. New compaction methods, from die-wall lubrication to the so-called warm compaction are now industrial realities. As to production equipment, PM part makers progressively require and introduce new presses and new furnaces. Even if a comparison between different equipment may be controversial, it seems hard to deny that press manufacturers proceeded at a higher speed in comparison to furnace makers. By and large, the most modern presses are definitely more sophisticated and effective than the equipment available 20 years ago. The evolution of sintering equipment proceeded at a slower pace, even if the progress achieved in devices to be used for controlling protective atmospheres is unquestionable. The most advanced systems suitable to analyze controlled atmospheres may today utilize high stability infrared detectors, for the simultaneous measurement of carbon monoxide, carbon dioxide and methane. In addition, the analysis can also be supplied with a methane-compensated thermal conductivity cell for hydrogen. A separate oxygen detector can also be supplied for measuring low (ppm) or percentage levels of oxygen in the gas sample. All detected gases have a separate digital readout and linear recorder output.

As to “revolutionary” design changes (comparable with the introduction of numerically controlled multi-platen presses, now proposed by any press supplier), the offer of “revolutionary” furnaces appears limited. A Japanese furnace, equipped with carbon belt, and apt to operate up to 1400°C seems a remarkable novelty. The different chemical requirements that characterize the various zones of a sintering equipment, clearly analyzed for instance by Kaufman [38], and Nayar [39,40], addressed only few furnace manufacturers to investigate and develop new – and reliable – technical solutions, suitable to transform equipment from a unique but multi-purpose chemical reactor to a succession of “dedicated” and different chemical reactors. Presumably, the growing application of sophisticated sintered steels, achieved by sinter hardening, will impose a more accurate control of carbon content and will contribute to bringing on this possible evolution.

Some furnace manufacturers might judge provocative and even hurtful, the previous statements. Definitely, the author’s intention was not to be insulting, but to call the attention of far-sighted furnace makers for challenging opportunities.

CONCLUDING REMARKS

Considering the previous analyses and evaluations, some basic remarks may be drawn:

- Interactions between controlled atmospheres and ferrous materials during sintering can be evaluated and predicted, with a good approximation, by suitable calculations.
- The classical concept of chemical equilibrium holds only for small volumes, mostly on surface zones of the parts.
- The different physical properties of gases that constitute the different atmospheres play a significant role on the results of sintering inside the components, namely “at the part core”.
- Any change of gas composition corresponding to equilibria at different temperatures, occurs at the speed which characterizes the kinetics of reaction. Therefore, even if some equilibrium indicates risks or advantages, the real situations and final conditions may be quite far away from the expected equilibria.
- The core of high-density and big and massy parts can result badly sintered, due to the lack of access for the reducing agents of the atmosphere. Unfortunately, no data concerning the interactions between part geometry, density and effectiveness of the reduction mechanisms in different sintering situations are available in the literature. At least in principle, it should be possible to define and detect a “reduction depth”, analogous to the carburizing depth for heat treatments. Other conditions being equal, this reduction depth should decrease as far as the part density increases.
- Hydrogen has the highest diffusive mobility of any other constituent of controlled atmospheres.
- As a rule, hydrogen is not decarburizing, at least below 1150°C. At higher temperatures, in the presence of carbon, even if the equilibrium indicates a low tendency towards decarburizing, this unwanted reaction may occur rather rapidly. In principle, hydrogen can protect carbon against the take-away action due to the oxygen corresponding to the H₂-loss of the base powder. Some PM engineers believe that H₂ tends to segregate in the higher regions of the muffle, due to the density difference in comparison with any other atmosphere constituent. This tendency for gas layering inside a muffle, starting from a homogeneous mixture, seems to be against the second law of thermodynamics and the corresponding principle of entropy increase. However, the controlled atmosphere slowly flowing inside a sintering furnace is completely far away from a closed system, and a lot of energy exchanges occur which involve the circulating gases. Since any layering brings about a decay of atmosphere properties, the opinion of some sintering engineers should be checked by means of a careful chemical mapping of typical equipment.
- The correct sintering of PM steels requires suitable equipment. A carbon restoration zone is compulsory in the case of an endogas (or methanol) atmosphere.
- If the hydrogen loss of the base powder is constant and low enough, the graphite additions may be suitably adjusted to compensate for the carbon loss due to oxygen removal.
- The furnace manufacturers should supply the typical thermal profiles of their equipment, made at different furnace loadings and with different atmosphere flow-rates.
- For a more accurate mastering of sintering processes, part manufacturers should investigate the chemical profiles inside furnaces to be used for demanding productions. Even if measured data may be different from the actual compositions inside furnaces,

the consistency of results should enable one to assure the consistency of process conditions and material properties, namely, material' quality.

- The flow pattern of atmosphere motion inside a sintering furnace is still partially unknown. The furnace makers should supply information on typical flow patterns, at different atmosphere flow-rates and for various thermal profiles. For cost-effectiveness, the gas flow-rate should be as low as possible. As a rule of thumb rule, we can assume that for a customary belt furnace with a horizontal axis, each cm of belt width requires 1 nm³/hour of atmosphere. This flow-rate should prevent any uncontrolled air inlet from both the furnace extremities. The corresponding Reynolds number however, shows that flow pattern, at least at a certain distance from the intake point, should be viscous. Then the lack of whirls could at least partially agree with the idea of layering between constituents inside the gaseous mixture.
- A new type of atmosphere, named Alnat I by the producer, could replace endogas with some positive fall-out on production costs and on material properties. Possible negative effects due to composition changes, when the atmosphere is “slowly” heated from 700 K to sintering temperature, should be checked by practical tests.
- With properly engineered sintering furnaces, equipped with a controlled fast-cooling section, the tolerance on carbon can be reduced and optimum microstructure for PM steels of any given composition can be achieved.
- The new iron-base powders, which justify the terms “sinter hardening” or “sinter-quenching”, can be correctly and advantageously sintered in furnaces equipped with the various chambers provided for specific functions and exhibiting the required thermal profiles. They will serve to narrow the ranges of carbon content on PM steels.
- A stricter co-operation between part manufacturers, furnace makers and sintering experts can enhance the possibilities of using improved PM steels for reliable and advanced applications.
- PM parts which require machining – for shape peculiarities – and induction hardening – for improving wear resistance, may be seen as a “litmus paper” to rate the capability of PM part makers to get consistent results when producing sintered steels. As a matter of fact, the needs of machining work out an upper limit to carbon content, whereas the need of hardenability establish a lower limit to carbon content. In general, the gap between upper and lower limits on carbon content is modest, limited to less than 0.2%. Only PM part makers that really master the sintering of steels and can utilize advanced, reliable, and properly controlled equipment can fulfil those demanding requirements.
- The growth of PM applications depends also on a continuous decrease of differences, with respect to fully dense steel. To progress in this direction, tolerance ranges on carbon content must be narrowed. Today, any comparison between conventional steels and PM steel is unfavourable to powder metallurgy. Since a remarkable narrowing of carbon ranges is possible, this direction is a strong push for improvement, at least for progress-oriented furnace makers and PM part manufacturers

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