DOI: 10.24425/amm.2020.132831

M. SUŁOWSKI[1*], M. TENEROWICZ-ŻABA[1], R. VALOV[2], V. PETKOV[2]

SINTERED Ni-FREE STRUCTURAL ALLOY STEELS – PROCESSING, PROPERTIES AND MICROSTRUCTURE

In this paper the development and method of production of modern, Ni-free sintered structural steels containing Cr, Mn and Mo, enabling the production of structural sintered steels in industrial conditions, using safe, with low H_2-content, sintering atmospheres is presented. For this purpose, the analysis of microstructure and mechanical properties of these sintered structural steels produced in different processing conditions and also the connections between the microstructure of sintered material and its mechanical properties, was presented. Following the investigations, the appropriate chemical composition of sintered Ni-free steels with properties which are comparable or even better than those of sintered structural steels containing rich and carcinogenic nickel was choosen. Additionally, in the paper the properties of electrolitically coated carbon steels were presented, as the beginning of investigation for improving the mechanical properties of alloyed, structural sintered steels.

Keywords: sintered Ni-free alloy steels, sintering atmosphere, mechanical properties, microstructure

1. Introduction

Powder metallurgy (PM) steels are differ from their wrought counterparts. The alloying elements such as Ni and Cu, and sometimes Mo have traditionally been used in high-strength sintered structural steels. Mn has a great effect on hardenability but its use in PM is very restricted because of its strong affinity for oxygen [1]. On the other hand these alloying elements are more effective than additions of Mn, because their oxides are reducible during sintering in standard industrial conditions (1120°C, dissociated ammonia atmosphere, –30°C dew point). Nevertheless, the PM industry is interested in developing Ni-free PM steels, characterised by mechanical properties as high as diffusion alloyed Ni-containing sintered steels and also fulfill the requirements of health protection [2].

During last 70 years, sintered manganese steels, especially structural PM steels, have been the interests of scientists from all over the world. The main objects of the researches concerned: a) the effect of Mn concentration and other alloying elements on the mechanical properties of PM structural parts, b) the effect of alloying elements, on the microstructure and mechanical properties of sintered Mn steels and c) elimination of Ni and Cu by introducing in sintered steels Mn and Cr causing to increase the mechanical properties of PM Mn steels [3-21].

2. Experimental materials

During investigations the following powders were used as the starting materials:

- Höganäs iron powder grade NC 100.24 (sponge),
- Höganäs pre-alloyed iron powders: Astaloy Mo (Fe-1.5%Mo), Astaloy CrL (Fe-1.5%Cr-0.2%Mo), Astaloy CrM (Fe-3%Cr-0.5%Mo),
- low-carbon (Fe-77%Mn-1.18%C) (delivered by Elkem Eramet Norway) and high-carbon, low-silicon (Fe-73%Mn-6.25%C0.71%Si) ferromanganese powders,
- Höganäs graphite powder grade C-UF.

From these powders mixtures with compositions of:

- Fe-(3-4)%Mn-0.8%C, Fe-(3-4)%Mn-0.5%Mo-(0.6-0.8)%C and Fe-0.5%Mo-(0.6-0.8)%C,
- Fe-(0.2-0,8)%C, Fe-3%Mn-(1.5-3)%Cr-(0.2-0.5)%Mo-(0.3-0.8)%C and Fe-(1-3)%Mn-0.8%C

were double cone and Turbula mixed for 60 and 30 minutes, respectively. To obtain similar green density of compacts, single-action pressing, at 810 and 660 MPa was introduce to prepare green compacts 5×10×55 mm and according to PN-EN ISO 2740 standard, respectively. Both green and as-sintered densities were in the range 6.5-7.0 g/cm^3. Zinc stearate was used as a lubricant and was applied on the punches before pressing each sample.

[1] AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AL. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND
[2] INSTITUTE OF METAL SCIENCE, EQUIPMENT AND TECHNOLOGY WITH HYDROAERODYNAMIC CENTER "ACAD. ANGEL BALEVSKI" AT BULGARIAN ACADEMY OF SCIENCES, 67 SHIPCHENSKI PROHOD STREET, 1574 SOFIA, BULGARIA

* Corresponding address: sulek@agh.edu.pl

Sintering was carried out in a semi-closed container proposed in [22] at different sintering temperature (ST):

- ST at 1120°C of the Fe-(0.2-0.8%C) with dew point: –60ºC,
- ST at 1120°C, 1150°C, 1180°C, 1200°C of the Fe-(3-4)% Mn-0.8%C steels with different atmosphere dew point varied from –40°C up to –60°C,
- ST at 1220°C of the Fe-(3-4)%Mn-0.5%Mo-(0.6-0.8)%C and Fe-0.5%Mo-(0.6-0.8)%C steels with dew point: –60ºC,
- ST at 1120°C and 1250ºC of the Fe-(1-2.5)%Mn-0.8%C steels and steels based on Astaloy pre-alloyed powders with dew point: –60ºC

for 60 minutes in pure N_2, pure H_2 and mixtures thereof (from 5%H_2 to 75%H_2). Both gases had quality standard 5.0 (purity 99.999%). Heating rate to sintering temperature was 75ºC/min. Following sintering, four types of heat treatment were employed: sinterhardening (SH; cooling rate (CR) = 66°C/min.), sinter-hardening (SH+T; CR = 66°C/min. and tempering temperature TT = 200°C), slow furnace cooling (SC; CR = 3.5ºC/min.) and industrial cooling rate (IC; CR ~ 10ºC/min.). The average cooling rates (SH, SC and IC) were calculated for all sintering temperatures in the range of 1100°C-500°C. Additionally, on carbon Fe-(0.2÷0.8)%C PM steels, electrochemical Cr coatings doped with diamond nanoparticles (ND) were produced by detonation synthesis were deposited. This coatings were prepared to increase the mechanical properties of carbon steels. On the other hand, the use of such layers on the alloy steels it is planned. The electrolytic conditions were as follows: electrolyte containing CrO_3 – 220 g/l and H_2SO_4 – 2.2 g/l, current density – 45 A/dm^2; duration of the process – 45 minutes and temperature of the electrolyte – 50°C. The ND were added to the electrolyte as an aqueous suspension at concentrations (C_{ND}) of 10, 25 and 42 g/l.

3. Experimental methods

The steels were physically and mechanically tested at room temperature. Green and as-sintered (as-tempered) densities were calculated by the geometric methods. Tensile testing was carried out on MTS 810 machine (USA) at a cross-head speed of 1 mm/min. Tensile (UTS) and bend (TRS) strengths were calculated according to PN-EN ISO 6892-1:2016-09 and PN-EN ISO 3325 standards, respectively. Bend strength was measured using ZD10-90 (Fritz HECKERT, Germany) and WDW-Y300D (Zhongke, China) testing machines. Hardness was investigated on the macroscale (surface hardness) on WPM Vickers/Brinell hardness tester and on the microscale (cross-sectional hardness) on an Innovatest tester using the Vickers method. Impact test (KC) was carried out at room temperature using 55×10×5 mm specimens and a 15 J Charpy bar impact tester according to the PN-EN ISO 148-1:2010 standard (samples were placed on supports with a distance of 25 mm). The number of tested samples in each batches was 10 or 15 (mean value for 10 or 15 samples). Following mechanical tests, metallographic and fracture investigations were carried out using Leica DM 4000M and JEOL JSM 700F microscopes, respectively. For metallographic investigations samples were prepared according to the procedure described in [23].

4. Results and discussion

4.1. The mechanical properties of 1-3%Mn PM steels

The first work describing the usage of Mn in PM steel appeared in 1950 published by F. Benesovsky and R. Kieffer [24] and, followed by, in 1968 and 1971, K. Mauer and H. Grewe [25]. Sintered Fe-Mn compacts were also precisely investigated by G. Zapf et al [26], who reported the best combination of mechanical properties (yield point, tensile strength) at ~6%Mn. Very important investigations were done by A. Salak [27], who discover and first described the self-cleaning effect of Mn vapour.

Following work done by Salak [27], the investigations described in e.g. [28-30] allowed the establish the most favourable chemical compositions of the powder mixtures. As a result of these investigations, the following powders were chosen: Höganäs sponge iron powder grade 100.24 and Elkem low-carbon (1.18%C) ferromanganese. The results obtained show the influence of sintering temperature and Mn content on mechanical properties of the investigated steels (Table 1 and 2).

The data pesented in Table 2 show that for sintered steel containing 2-3% Mn, higher strength and elongation could be obtained than in the PM (Ni)-(Cu)-(Mo) alloyed steels described

TABLE 1

Mechanical properties of sintered Fe-(1-3)%Mn-0.8%C steels – mean values and corrected standard deviations (15 samples per variant) [29]

Chemical composition	Sintering variant	$Rp_{0,2}$ offset, [MPa]	UTS, [MPa]	TRS, [MPa]	A, [%]	HV 0.05 (cross-section)
Fe-1%Mn-0.8%C[27]	1120°C/SH	285±23	511±22	888±85	4.36±0.5	240±54
	1250°C/SH	297±45	587±32	1070±95	5.80±0.54	241±43
Fe-1.5%Mn-0.8%C	1120°C/SH	371±43	580±55	1005±115	4.13±0.73	250±21
	1250°C/SH	370±25	632±39	1132±84	4.92±0.54	226±11
Fe-2%Mn-0.8%C[27]	1120°C/SH	367±22	611±22	997±85	3.73±0.54	310±66
	1250°C/SH	429±31	713±53	1200±88	4.23±0.60	429±55
Fe-2.5%Mn-0.8%C	1120°C/SH	501±44	671±31	997±120	3.34±0.33	287± 53
	1250°C/SH	623±75	754±61	1187±110	3.66± 0.43	270± 36
Fe-3%Mn-0.8%C[27]	1120°C/SH	529±29	626±81	1112±108	2.95±0.30	390±131
	1250°C/SH	602±42	727±48	1234±130	3.35±0.35	343±87

TABLE 2

Mechanical properties of Fe-2.5/3%Mn-0.8%C with those of the most demanding PM steels of MPIF Standard 35 [31]: FC-0208-60, FC-0508-60, FN-0408-55 and FLN-4205-55 with yield strengths above 400 MPa (15 samples per variant)

Steel designation/ description		Chemical composition%, balance Fe					Mechanical properties						
		C	Ni	Cu	Mo	Mn	Density, [g/cm^3]	$Rp_{0,2}$ offset, [MPa]	UTS, [MPa]	A, [%]	TRS, [MPa]	Hardness	Ref.
Fe-Cu	FC-0208-60	0.6-0.9	—	1.5-3.9	—	—	7.2	450	520	<1	1070	84 HRB	31
Fe-Cu	FC-0508-60	0.6-0.9	—	4-6	—	—	6.8	480	570	<1	1000	80 HRB	31
Fe-Ni	FN-0408-55	0.6-0.9	3-5	0-2	—	—	7.2	410	550	1	1030	87 HRB	31
Hybrid	FLN-4205-55	0.4-0.7	1.3-2.5	—	0.49-0.85	0.2-0.4	7.3	430	600	2	1210	83 HRB	31
2Mn	1250°C / SH	0.8	—	—	—	2	6.6	430	710	4.2	1200	429 HV	32
3Mn	1120°C / SH	0.8	—	—	—	3	6.6	600	730	3.4	1234	345 HV	32
3Mn	1250°C / SH	0.8	—	—	—	3	6.6	530	630	3.0	1110	390 HV	32
3Mn	1120°C / SH	0.8	—	—	—	3	6.9	410	500	1	1230	183 HV	30
3Mn	1120°C SH+T	0.8	—	—	—	3	7.0	410	740	2.3	1740	250 HV	30
3Mn	1250°C / SH	0.8	—	—	—	3	7.0	480	610	1.2	1310	189 HV	30
3Mn	1250°C / SH+T	0.6-0.7	—	—	—	3	6.9	450	730	1.6	1234	266 HV	33
3Mn	1250°C / SH	0.8	—	—	—	3	7.0	460	480	1.5	1060	210 HV	30
3Mn	1250°C / SH+T	0.8	—	—	—	3	6.7	470	830	3.7	1480	247 HV	30
2.5Mn	1120°C / SH	0.8	—	—	—	2.5	6.5	500	670	3.3	1000	287 HV	28
2.5Mn	1250°C / SH	0.8	—	—	—	2.5	6.5	620	750	3.7	1190	270 HV	28

in literature [31]. This shows the possibility of substitiution carcinogenic Ni and Cu with Mn structural sinterhardened steels used today.

The microstructure of investigated steels [28-30] changed with the amount of Mn: from mainly pearlite and ferrite, sometimes bainite – which was observed in Fe-1%Mn-0.8%C PM steels – through pearlitic, bainitic and martensitic, in the areas surrounding the residual particles of ferromanganese, up to martensitic or bainitic/martensitic with Mn-rich austenite for Fe-3%Mn-0.8%C. This modification is connected with the increasing influence of Mn on creation of martensitic (bainitic/martensitic) structure.

4.2. The effect of cooling rate and chemical composition of sintering atmosphere on microstructure and mechanical properties of Mn PM steels

The effects of cooling rate from the sintering and the tempering temperature on the microstructure and mechanical properties of PM Mn alloyed steels were described [34]. It is well known that mechanical properties of sintered steels, especially UTS and TRS, increase with decreasing dew point of the sintering atmosphere. Decreasing of sintering atmosphere dew point allows an increase of toughness and surface hardness of the investigated steels.

Cooling rate had a great influence on mechanical properties of investigated steels (Table 3); when decreasing of cooling rate from sintering temperature sometimes increases mechanical properties by a factor of up to two. The plasticity of the investigated steels increase with decreasing cooling rate: for slow colled sintered steels their elongation after tensile test was about 3.8%, which in the case of PM steels is a more than satisfactory value (Table 3).

The aim of work described in [34] was also to show if sintering of structural steels containing element(s) with high affinity for oxygen is possible in an atmosphere with a low amount, or even free, of hydrogen. On the basis of the results showed in Table 4 it can be concluded that the change in the chemical composition of the sintering atmosphere from mixture of H_2-N_2

TABLE 3

Mechanical properties of Fe-3%Mn-0.8%C PM steels; sintering atmosphere – 100% H_2, dew point –60°C – mean values and corrected standard deviations (10 samples per variant) [34]

Composition	Sintering temperature 1120°C						
	Cooling	UTS, [MPa]	TRS, [MPa]	HV30 cross.	KC, [J/cm^2]	$Rp_{0,2}$ offset, [MPa]	A, [%]
NC 100.24 + Elkem + C-UF	SC	478±43	1272±62	224±63	17.22±0.9	380±40	3.04±0.2
	IC	506±54	1230±94	217±79	10.86±1.0	414±57	3.08±0.2
	SH	642±22	1279±68	236±54	4.68±0.8	—	1.87±0.2
	Sintering temperature 1250°C						
	Cooling	UTS, [MPa]	TRS, [MPa]	HV30 cross.	KC, [J/cm^2]	$Rp_{0,2}$ offset, [MPa]	A, [%]
	SC	595±40	1327±70	254±43	11.50±0.5	461±25	3.80±0.2
	IC	614±45	1311±88	239±52	9.92±0.8	477±48	2.87±0.2
	SH	717±25	1296±54	315±30	5.04±1.0	—	1.60±0.2

TABLE 4

Mechanical properties of Fe-3%Mn-0.8%C PM steels – mean values and corrected standard deviations (10 samples per variant) [34]

Composition	Cooling	H_2 in N_2-H_2 mixture, %	UTS, [MPa]	TRS, [MPa]	HV30 cross.	KC, [J/cm^2]	$Rp_{0,2}$ offset, [MPa]	A, [%]
Sintering temperature = 1120°C, dew point –60°C								
NC 100.24 + Elkem + C-UF	SH	100	642±22	1279±68	236±54	4.68±0.8	386±40	1.87±0.2
		75	640±45	1291±55	247±29	5.09±0.8	400±34	1.79±0.2
		25	650±51	1299±95	226±32	7.44±0.9	420±65	1.78±0.2
		5	657±65	1234±101	186±46	7.27±0.8	421±73	1.82±0.2
		0	655±70	1259±62	202±30	14.31±0.9	410±53	1.93±0.2
Sintering temperature = 1250°C, dew point –60°C								
Composition	**Cooling**	**H_2 in N_2-H_2 mixture, %**	**UTS, [MPa]**	**TRS, [MPa]**	**HV30 cross.**	**KC, [J/cm^2]**	**$Rp_{0,2}$ offset, [MPa]**	**A, [%]**
NC 100.24 + Elkem + C-UF	SH	100	717±25	1296±54	315±30	5.04±1.0	426±44	1.60±0.2
		75	749±44	1343±68	295±35	13.30±1.0	443±56	1.71±0.2
		25	778±34	1411±120	298±63	10.83±0.9	459±34	1.82±0.2
		5	725±56	1420±94	266±44	12.45±1.0	451±25	1.67±0.2
		0	776±65	1458±87	260±51	13.23±1.0	464±30	2.00±0.2

to pure N_2 does not influence significantly the mechanical properties of these steels.

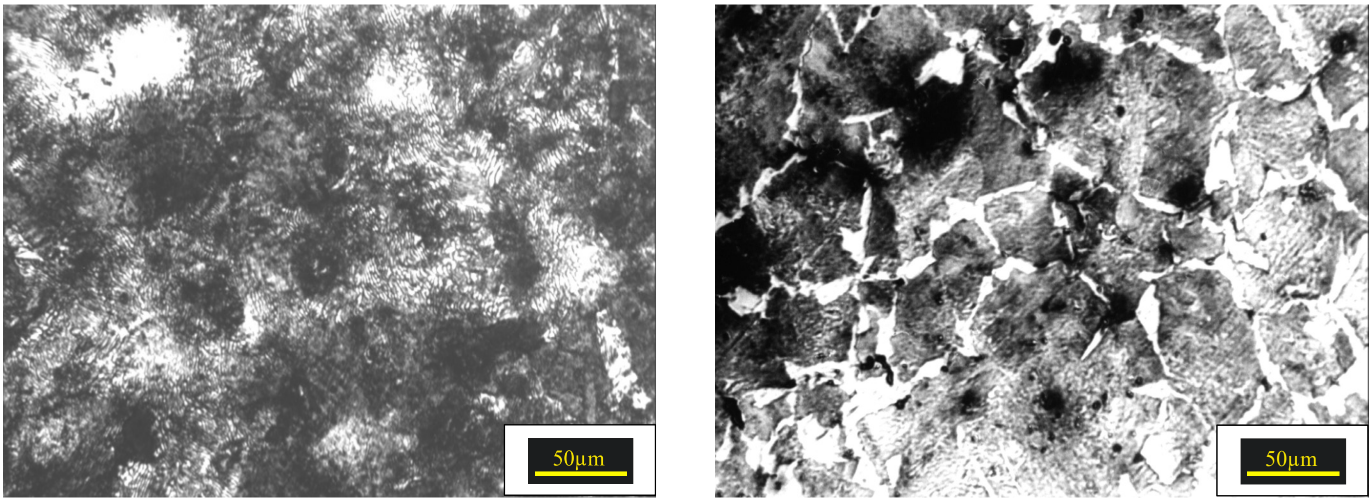
Following metallographic observation it can be concluded that the microstructure of steels investigated in [34] depended on the sintering temperature and cooling rate from the sintering temperature. Slow cooling rate, regardless of the sintering temperature, contributed to the formation of pearlitic structure. Increasing the cooling rate resulted in: first fine pearlite, then acicular bainite with martensite, and finally acicular bainite with martensite and retained austenite (Table 5, Figs. 1 and 2).

During investigations described in [34] the fracture surfaces of PM Mn steels were observed. From these results obtained it can be concluded that sinterhardened steels were characterized by transgranular brittle fracture; their elongation – from stress-strain curve – was about 0.1%. Sometimes, because of thin "oxide film" located on grain boundaries of austenite, the fracture was intergranular. However, for steels produced in SH+T variant, their fracture was changed from brittle to transgranular ductile fracture; in this case their elongation was up to 4%.

TABLE 5

Microstructural constituents of Fe-3%Mn-0.8%C PM steels vs. cooling rate and sintering temperature (ST) [34]

Cooling	ST = 1120°C	Cooling	ST = 1250°C
SC	Pearlite	SC	Pearlite + proeutectoid ferrite
IC		IC	
SH	Acicular bainite + martensite + retained austenite	SH	Acicular bainite + martensite + retained austenite
SH+T	Martensite + retained austenite	SH+T	Martensite + retained austenite



a) b)

Fig. 1. Photomicrograph of Fe-3%Mn-0.8%C PM steels; ATM = 100% H_2, DP = –60°C; CR = 5°C/min. [34]: a) 1120°C, SC; pearlite, b) 1250°C, SC; pearlite and ferrite

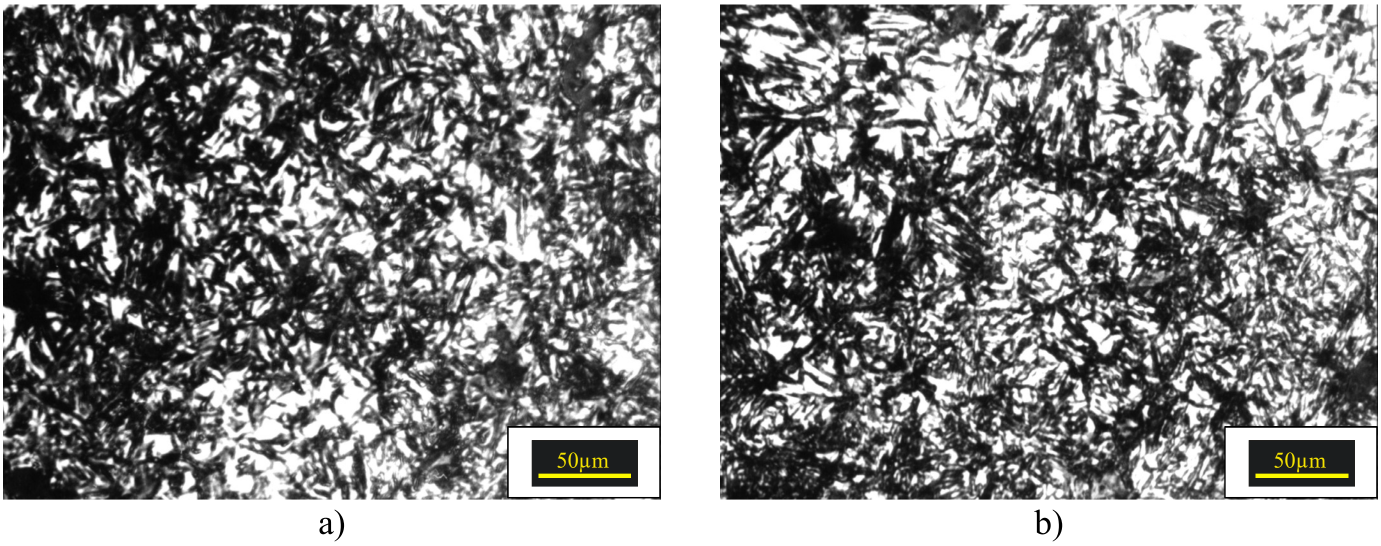


Fig. 2. Photomicrograph of Fe-3%Mn-0.8%C PM steels ATM = 100% H_2, DP = –60°C [34]: a) 1120°C, SH; bainite, martensite and retained austenite, b) 1250°C, SH; bainite, martensite and retained austenite

4.3. PM alloyed steels containing manganese, molybdenum and silicon

Molybdenum is one of the important alloying elements very often used in PM Fe-based materials. Its addition to PM steel causes solid solution hardening and increases both tensile strenght and hardness without decreasing plasticity of the steel (Table 6). Because of it, Mo, when together with Mn, is a very important factor which decides the hardenability of sintered steels [27,34,35].

Silicon is cheaper than Mo, Cr, Cu or Ni and has a positive effect on the strength properties of sintered steels. It also has a stabilizing effect on ferrite and use affects the sintering process with a liquid phase at high carbon contents. The affinity of silicon for oxygen is greater than that of copper, nickel or molybdenum [36].

From Table 6 can be found that Mn-Mo steels can be designated as medium-to-high strength steels (UTS = 640 MPa, $Rp_{0.2}$ yield offset = 535 MPa). The lack of Mn in the composition of PM steels mentioned in Table 6, had an unfavourable influence on their properties. The results show that sintered Mn-Mo steels had rather good plasticity the elongation after tensile test did not exceed 3%. The microstructure of Mn-Mo PM steels was inhomogeneous and mainly consisted of bainite, martensite and Mo-rich ferrite. The most important conclusion was that mechanical properties of the PM Mn-Mo steels after sintering in H_2 were comparable with those of steels sintered in N_2, which confirmed previous investigations [27,34,35].

4.4. Effect of chemical composition of Fe-Cr-Mo-Mn sintered steels

The effect of processing parameters, especially chemical composition of the sintering atmosphere and the sintering temperature, on the microstructure and mechanical properties of PM Fe-3%Mn-(1.5-3)%Cr-(0.2-0.5)%Mo-0.3%C structural steels was reported in [37] and summarized in Table 7.

TABLE 6

The properties of PM steels – ST at 1220°C, 1 h – mean values and corrected standard deviations (15 samples per variant) [35]

Chemical composition / sintering atmosphere	UTS, [MPa]	$Rp_{0.2}$ offset, [MPa]	A, [%]	TRS, [MPa]	HV 30 cross.
Fe-3Mn-0.6C-0.5Mo-0.03Si / N_2	639±40	535±40	2.99±0.1	1253±55	255±39
Fe-3Mn-0.6C-0.5Mo-0.03Si / H_2	659±43	453±43	2.70±0.2	1164±58	250±30
Fe-3Mn-0.8C-0.5Mo-0.04Si / N_2	600±46	385±35	2.83±0.2	1390±67	312±45
Fe-3Mn-0.8C-0.5Mo-0.04Si / H_2	635±78	417±87	2.88±0.1	1205±99	285±53
Fe-4Mn-0.6C-0.5Mo-0.04Si / N_2	535±49	385±35	1.60±0.1	954±101	281±29
Fe-4Mn-0.6C-0.5Mo-0.04Si / H_2	564±39	369±45	1.71±0.1	1092±76	301±44
Fe-4Mn-0.8C-0.5Mo-0.04Si / N_2	455±76	—	1.10±0.2	1032±66	280±64
Fe-4Mn-0.8C-0.5Mo-0.04Si / H_2	467±55	384±64	1.23±0.2	985±75	224±35
Fe-0.5Mo-0.6C / N_2	486±36	351±55	2.32±0.2	982±102	133±58
Fe-0.5Mo-0.6C / H_2	466±57	359±22	1.97±0.2	921±66	165±43
Fe-0.5Mo-0.8C / N_2	541±73	383±38	2.34±0.1	1041±73	151±64
Fe-0.5Mo-0.8C / H_2	512±44	350±43	2.14±0.1	964±85	163±54

TABLE 7

Mechanical properties of Fe-Mn-Cr-Mo-C PM steels (SH) – mean values and corrected standard deviations (15 samples per variant) [37]

Sintering temperature, °C and atmosphere		UTS, [MPa]	$Rp_{0.2}$ offset, [MPa]	A, [%]	TRS, [MPa]	KC, [J/cm^2]	HV 30 surf.
Fe-3%Mn-1.5%Cr-0.2Mo-0.3%C							
1120	75%H_2-25%N_2	512±60	428±90	1.3±0.4	907±91	3.2±1.0	190±29
	25%H_2-75%N_2	438±47	361±35	0.9±0.4	1042±122	2.1±0.7	207±34
	5%H_2-95%N_2	400±70	429±30	0.8±0.3	691±420	2.2±1.0	247±64
	100 % N_2	374±22	285±73	0.7±0.2	922±154	2.0±0.8	229±48
Fe-3%Mn-3%Cr-0.5Mo-0.3%C							
1120	75%H_2-25%N_2	584±59	498±32	1.1±0.2	987±63	3.1±1.0	255±46
	25%H_2-75%N_2	532±32	451±67	1.1±0.2	1036±81	3.0±1.0	302±49
	5%H_2-95%N_2	515±26	386±6	1.0±0.2	915±68	2.7±1.0	341±29
	100 % N_2	495±34	479±34	1.0±0.2	965±55	3.0±0.9	353±40
Fe-3%Mn-1.5%Cr-0.2Mo-0.3%C							
1250	75%H_2-25%N_2	602±50	398±61	1.6±0.4	1027±140	4.4±0.9	260±46
	25%H_2-75%N_2	510±39	466±31	1.1±0.3	1214±83	4.5±1.2	249±63
	5%H_2-95%N_2	456±79	484±53	0.8±0.4	1148±146	3.0±1.1	235±30
	100 % N_2	466±58	429±32	1.2±0.3	970±68	3.0±1.3	225±34
Fe-3%Mn-3%Cr-0.5Mo-0.3%C							
1250	75%H_2-25%N_2	816±68	587±16	2.5±0.1	1454±73	5.5±0.9	326±51
	25%H_2-75%N_2	672±66	569±34	1.5±0.1	1153±69	3.6±0.8	345±40
	5%H_2-95%N_2	572±163	526±22	1.1±0.3	1041±119	3.7±0.9	351±43
	100 % N_2	670±82	—	2.0±0.3	1061±84	2.9±1.0	362±32

The microstructure of PM Mn-Cr-Mo-C steels consisted mainly of martensite, bainite and austenite and their percentage depends on the processing parameters. For higher concentrations of Cr and Mo [38], sintering at 1200°C in N_2 atmosphere had to be employed to improve strength properties. The UTS, TRS, and A values, calculated for specimens sintered at 1200°C were, by 6%, 4% and 6%, higher than the values obtained for specimens sintered at 1120°C (Table 8).

The microstructure analysis of PM Fe-Mn-Cr-Mo-C steels sintered in H_2 shows the evidence of decarburization and higher porosity in the subsurface layer of specimens, irrespective of the sintering conditions (Fig. 3a). Such phenomena was also observed by Bowe et al [39].

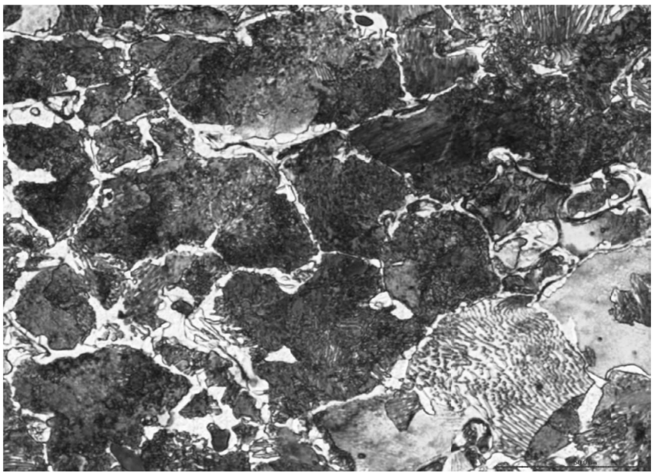
The steel containing 3% Cr and 0.5% Mo, sintered at 1120°C in N_2 and sinterhadened (SH), were characterised by pearlitic and bainitic structure. There were few big clusters of tempered martensite and retained austenite, and undissolved particles of ferromanganese and slag inclusions dispersed in a fine-grained microstructure. After sintering at 1200°C, steels were characterised by mainly acicular bainite, tempered martensite and retained austenite (e.g. Fig. 3b), although pearlitic/bainitic regions and undissolved particles of ferromanganese were also observed.

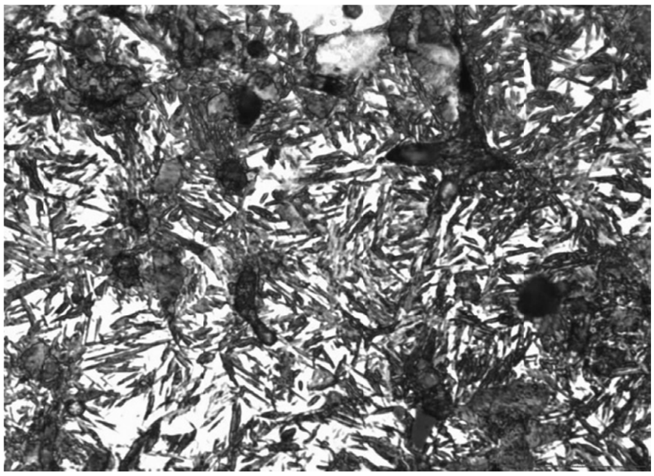
The steel containing 1.5% Cr and 0.25% Mo, had much more homogeneous microstructure. After sintering at 1120°C in N_2, ferritic/pearlitic regions in the subsurface were localised,

TABLE 8

Mechanical properties of Fe-Mn-Cr-Mo-C PM steels [38]

Sintering temperature, °C and atmosphere		UTS, [MPa]	$Rp_{0.2}$ offset, [MPa]	A, [%]	TRS, [MPa]	KC, [J/cm^2]	Hardness HV30 measured on: Surface	Hardness HV30 measured on: Cross-section
Fe-3%Mn-1.5%Cr-0.25%Mo-0.8%C								
1120	100%N_2	582±72	275±73	4.4±0.2	1138±95	12.0±0.9	186±40	213±35
	100%H_2	612±60	292±90	4.2±0.2	1282±84	11.6±0.8	195±63	227±48
1200	100 %N_2	723±58	267±67	4.2±0.1	1470±68	8.7±0.8	257±48	239±62
	100 %H_2	766±66	260±45	4.3±0.1	1554±75	14.5±0.9	229±55	265±59
Fe-3%Mn-3%Cr-0.5%Mo-0.8%C								
Sintering temperature, °C and atmosphere		**UTS, [MPa]**	**$Rp_{0.2}$ offset, [MPa]**	**A, [%]**	**TRS, [MPa]**	**KC, [J/cm^2]**	**Hardness HV30 measured on: Surface**	**Hardness HV30 measured on: Cross-section**
1120	100%N_2	613±34	273±34	4.2±0.1	1184±67	8.7±0.9	213±64	232±51
	100%H_2	671±46	284±52	4.2±0.2	1356±98	10.8±1.0	214±57	255±32
1200	100 %N_2	761±63	281±45	3.6±0.2	1529±76	12.0±0.8	248±36	250±46
	100 %H_2	720±45	280±22	3.4±0.1	1470±58	18.0±0.9	249±54	241±66





a) b)

Fig. 3. Microstructure of of Fe-3%Mn-3%Cr-0.5%Mo-0.8%C steel, sintered at 1120°C in a) N_2 (subsurface layer), b) H_2 (1000x, BF) [38]

whereas the core of the specimens consisted of fine pearlite and bainite. Increasing the sintering temperature did not influence the structure of the investigated steels. Steels sintered at 1120°C in H_2 show coarser microstructures containing pearlite, bainite and troostite, as well as – after sintering at 1200°C – tempered martensite and retained austenite.

Chemical composition of sintering atmosphere didn't influence on mechanical properties of the investigated steels. It follows that Mn-Cr-Mo steels can be successfully sintered in a N_2-rich atmosphere without decreasing their mechanical properties in comparision with steels sintered in H_2. As was shown in Table 9, sintering temperature affected strength and ductility of the sintered steel, irrespective of the alloy composition and sintering atmosphere.

Dilatometric investigations of Fe-Mn-Cr-Mo-C steels cooled at 20 °C/min. were described in [40]. Following this investigation it can be concluded that bainite transformation began at about 450-500°C and continued during cooling (Table 9). Martensitic transformation was not always complete before the finish of the dilatometric test. Cooling rate at 20°C/min. caused bainitic/martensitic transformation, to result in mainly martensite, bainite and austenite (also retained austenite) microstructures.

Compared with the data recorded for the 3%Mn+CrL specimens, the 3%Mn+CrM data showed slightly higher tensile and bend strengths [40]. Also, the yield strength, determined for the 3%Mn+CrM steels, was higher than that of the 3%Mn+CrL alloys, reflecting higher Cr content values (Table 10).

The various types of microstructure have been observed in various proportions in all the steels examined [40]. The as-sintered and as-tempered structures consisted of bainite and austenitic/martensitic regions. The investigations show also complex microstructures composed of bainite surrounding a large number of small, substantially unaligned, austenitic/martensitic areas, which are partially decomposed to carbide and ferrite.

The microstructure of PM steels strongly depended on the cooling rate after sintering [41]. Bainitic or bainitic/martensitic structure was formed during cooling at 30°C/min and 20°C/min after sintering at 1120°C and 1250°C, respectively, whereas pearlitc structure was observed after cooling with cooling rate lower than 20°C per minute [42].

4.5. The properties of electrolitically coated carbon steels, as the beginning of investigation for improving the properties of alloyed, structural sintered steels

Electrochemical Cr coatings doped with diamond nanoparticles (ND) produced by detonation synthesis were deposited on a powder metallurgy steel based on commercial NC 100.24 iron powder with different C contents (0.2, 0.4, 0.6 and 0.8 wt.-%)

TABLE 9

Continuous cooling transformation temperatures established by dilatometric analysis [40]

Sintering temperature, °C	Carbon content, %	Fe-3%Mn-1.5%Cr-0.2%Mo-(C)	Fe-3%Mn-3%Cr-0.5%Mo-(C)
	F_s ; P_s ; B_s transformation temperature, °C		
1120	0.3	F_s ; P_s = 850; 650	B_s ~500
	0.6	B_s ~ 500	M_s < 200
	0.8	B_s ~ 450	M_s < 200
1250	0.3	F_s ; P_s = 800;700	B_s ~ 500
	0.6	B_s ~ 500	B_s ~ 500
	0.8	B_s ~ 450	B_s~ 450

TABLE 10

Mechanical properties of CrL- and CrM based sintered steels – mean values [40]

Sintering			3%Mn+CrL+0.3%C					3%Mn+CrM+0.3%C				
°C	Atm.	CR	UTS, [MPa]	A, [%]	$Rp_{0,2}$ offset, [MPa]	TRS, [MPa]	KC, [J/cm^2]	UTS, [MPa]	A, [%]	$Rp_{0,2}$ offset, [MPa]	TRS, [MPa]	KC, [J/cm^2]
1120	H_2	SH+T	566±37	0.80±0.1	481±25	966±66	3.37±0.8	462±33	0.58±0.1	357±22	797±64	5.82±0.9
	N_2		556±44	0.82±0.1	481±34	995±75	3.40±0.8	716±29	2.53±0.1	535±25	1335±84	4.05±0.9
1250	H_2		608±53	1.16±0.2	474±46	1279±89	15.18±0.9	818±45	1.80±0.2	594±33	1492±65	6.55±0.8
	N_2		832±44	1.98±0.1	554±29	1325±85	15.25±0.8	957±53	2.75±0.1	562±42	1932±77	10.71±0.9
			3%Mn+CrL+0.6%C					3%Mn+CrM+0.6%C				
1120	H_2	SH+T	514±45	1.51±0.2	473±66	738±64	3.49±0.9	580±27	1.83±0.1	435±38	886±95	4.94±0.8
	N_2		544±29	1.50±0.1	539±57	1270±45	2.64±1.0	481±48	1.37±0.1	412±47	855±69	5.12±0.8
1250	H_2		729±32	2.68±0.1	547±31	1516±98	7.26±0.8	968±53	4.37±0.1	603±52	1734±66	11.22±1.0
	N_2		728±36	2.31±0.1	481±27	1503±83	4.27±0.8	925±29	4.00±0.2	548±42	2034±78	5.13±0.9
			3%Mn+CrL+0.8%C					3%Mn+CrM+0.8%C				
1120	H_2	SH+T	474±33	1.53±0.1	440±63	989±71	3.79±0.9	431±30	1.36±0.1	405±27	956±69	3.50±0.9
	N_2		431±51	1.18±0.3	474±35	950±63	3.34±0.9	389±45	1.31±0.2	360±31	929±79	4.51±0.9
1250	H_2		704±29	3.29±0.1	583±28	1435±58	8.25±0.8	887±62	4.56±0.2	536±38	1644±97	7.71±0.9
	N_2		684±33	2.58±0.1	432±42	1335±61	5.24±0.9	671±55	2.58±0.1	517±43	1303±89	8.63±1.0

added in the form of ultrafine graphite. Processing conditions of steel samples were: single pressing at 660 MPa followed by sintering at 1250°C in 5%H_2-95%N_2 mixture for 60 minutes. Heating and cooling rates were 75 and 60°C/min. After sintering, steel samples with geometry according to PN-EN ISO 2740, were electrolytically treated [43]. The mechanical properties of uncoated and Cr-coated sintered steels are presented in Tables 11-12.

The data in Tables 11 and 12 [43] indciate that increasing carbon concentration, of both uncoated and coated steels, mechanical properties increases, as reported in e.g. [44]. Regardless of chemical composition, strength properties (UTS, $R_{p0.2}$) were generally higher in coated than those of uncoated steels, but the presence of coating layer decreases ductility. The reason of such phenomena is the presence of Cr in the layer and its high affinity for carbon. The hardness layer, because of not clear tendency, should be investigated more deeply. On the other hand, mechanical properties coated steel samples are lower than those reported in e.g. [33,37,45] what is connected with absence of alloying elements in investigated steel.

5. Summary of the results

In the investigated steels, Cr, Mo and Mn elements were used as a substitution for Ni [2]. During the whole research, the route of sintering PM steels in semi-closed container (the microatmosphere effect) was employed [46]. During carrying out the work, the following sintering atmospheres were used: H_2, mixture of H_2 and N_2 with different N_2/H_2 ratios, pure N_2 and air (described in [28,33,34,36-38,41,47-53]). To compare the results, argon as sintering atmosphere was also introduced [52].

TABLE 11

The properties of uncoated steels – mean values (of 5 samples) and standard deviations [43]

Steel composition	As-sintered density, [g/cm^3]	UTS, [MPa]	$R_{p0,2}$ offset, [MPa]	A, [%]	Matrix hardness, HV 0.25	Friction coefficient
Fe-0.2%C	6.78±0.01	297±8	222±4	11.7±0.1	171-219	0.798±0.01
Fe-0.4%C	6.77±0.01	340±22	246±11	7.8±0.2		0.763±0.02
Fe-0.6%C	6.78±0.01	389±6	285±12	6.3±0.1		0.695±0.01
Fe-0.8%C	6.74±0.01	467±18	345±10	6.9±0.1		0.651±0.02

TABLE 12

The properties of coated steels – mean values (of 5 samples) and standard deviations [43]

Steel composition	As-sintered density, [g/cm^3]	UTS, [MPa]	$R_{p0,2}$, offset [MPa]	A, [%]	Layer hardness, HV 0.25	Matrix hardness, HV 0.25	Friction coefficient
Fe-0.2%C	6.78±0.01	331±9	242±13	8.9±0.1	774±62	171-219	0.517±0.01
Fe-0.4%C	6.77±0.01	366±28	297±8	6.1±0.8	667±84		0.505±0.02
Fe-0.6%C	6.78±0.01	405±3	376±16	5.0±0.1	648±86		0.582±0.01
Fe-0.8%C	6.74±0.01	442±20	404±17	4.3±0.3	856±65		0.523±0.01

Mn-Cr-Mo steels can be produced in H_2-low containing atmospheres or even in a pure N_2 atmosphere. Then their mechanical properties obtained after sintering in N_2-rich atmospheres are comparable with, or even better than, mechanical properties of the same steels sintered in a H_2-rich atmosphere. This can be related to "microclimate" effect in the boat in which the samples are sintered [53]. To adapt this phenomenon, semi-hermetic container and/or with a getter should be employed for production of Mn-Cr-Mo steels [22]. As was shown in [5], sintering of these steels is also possible in a container with a labyrinth seal in the presence of Al_2O_3 + Mn + C getter.

Usually in industrial conditions, sintering process is carried out for 30 or 60 minutes [54] and after it sintered compacts are cooled to room temperature. Because the investigated Mn-Cr-Mo steels contained elements increasing hardenability, during their processing an additional heat treatment – tempering at 200°C for 60 min. – was employed, what allowed for increase their mechanical properties by up to 30% [38,55].

Metallographic investigations showed that SH and SH+T sintered steels were characterized by high structural inhomogeneity. The microstructural constituents of investigated steels were ferrite, pearlite, upper and acicular bainite, austenite and martensite. The type of microstructure depended on the chemical composition of sintered steels and their processing parameters [34,56].

6. Conclusions

1. Steels sintered in N_2 atmosphere in comparison with those sintered in H_2 have satisfactory mechanical properties, which allow using this atmosphere during mass scale production of PM Fe-Mn-Cr-Mo-C steels.
2. Favourable combination of mechanical and plastic properties of PM Mn-Cr-Mo steels can be achieved after sinter-hardening and tempering at 200°C.
3. Investigated steels were characterised by an inhomogeneous microstructure depended on carbon concentration, sintering parameters and tempering conditions.
4. Decreasing Mn content in investigated steels up to 2.5% allowed for achieving high mechanical properties: 0.2% offset stress 623 MPa, UTS up to 750 MPa and 3.7% elongation.
5. The results of mechanical properties obtained for coated carbon steels are promising. The next step for testing electrolytically applied coatings should be strength tests carried out on coated alloy steels.

Acknowledgments

The work was realized as a part of fundamental research financed by AGH University of Science and Technology project number 16.16.110.663.

REFERENCES

[1] R.M. German, Powder metallurgy science, MPIF, Princeton, New Jersey (1984).
[2] EU Carcinogenic Directives 90/394/EEC and 91/322/EEC.
[3] S.C. Mitchell, A.S. Wronski, A. Cias, M. Stoytchev, Proc. of PM2TEC 1999, Vancouver, MPIF, Princeton **3**, part 7, 129-143 (1999).
[4] S.C. Mitchell, A.S. Wronski, A. Cias, Inżynieria Materiałowa **5**, 633-646 (2001).
[5] A.S. Wronski et al., Tough, Fatigue and Wear Resistance Sintered Gear Wheels. Final Report on EU Copernicus Contract no ERB CIPA-CT94-0108, European Commission (1998).
[6] M. Sulowski, A. Cias, Inżynieria Materiałowa **4** (105), 1179-1182 (1998).
[7] A. Cias, M. Sulowski, M. Stoytchev, Proc. of 7th European Conf. on Advanced Materials and Processes – EUROMAT 2001, June (2001).
[8] R. Keresti, M. Selecka, A. Šalak, Proc. Int. Conf. DFPM'99, IMR Kosice, SAS, Slovakia **2**, 108-111 (1999).
[9] S.C. Mitchell, B.S. Becker, A.S. Wronski, Proc. 2000 PM World Congress, EMPA, Kyoto **2**, part II, 923-926 (2000).
[10] A. Cias, M. Stoytchev, A.S. Wronski, Proc. 2001 Int. Conf. on Powder Metallurgy and Particulate Materials, MPIF, Princeton, New Jersey **10**, 131-140 (2001).
[11] A. Šalak, Powder Metallurgy International **16** (6), 260-263 (1984).
[12] A. Šalak, G. Leitner, W. Hermel, Powder Metallurgy International **13** (1), 21-45 (1981).
[13] J. James, B. Lindsley, B. Rutz, K.S. Narasimhan, Proc. Euro PM2009, EPMA, Copenhagen, Denmark **1**, 23-28 (2009).
[14] B. Lindsley, J. James, Proc. 2010 PM World Congress&Exhibition, EPMA, Florence, Italy, **3** - Sintered steels – Low alloy steels, 151-158 (2010).
[15] O. Bergman, S. Bengtsson, Proc. Euro PM2009, EPMA, Copenhagen, Denmark, **1** – Sintered steels II, 35-40 (2009).
[16] E. Dudrova, M. Kabatova, R. Bidulsky, A.S. Wronski, Powder Metall. **47** (2), 181-190 (2004).
[17] R. Bidulský, M.-A. Grande, Proc. 2010 PM World Congress&Exhibition, EPMA, Florence, Italy, **3 -** Sintered Steels - Mechanical properties, 95-102 (2010).
[18] E. Hryha, L. Nyborg, E. Dudrova, S. Bengtsson, Proc. Euro PM2009, EPMA, Copenhagen, Denmark, 1 - Sintered Steels I – Composition, 17-22 (2009).
[19] E. Hryha, L. Nyborg, Proc. Euro PM2013 EPMA, Gothenburg, Sweden, **2** - Sintering – Atmospheres and Atmosphere Control, 333-338 (2013)
[20] E. Hryha, L. Nyborg, L. Alzati, Proc. Euro PM2013, EPMA, Gothenburg, Sweden, **2** - Sintering – Fundamentals and Modelling, 303-310 (2012).
[21] C. Gierl-Mayer, E. Klammer, M. Dlapka, H. Danninger, Proc. Euro PM2013, EPMA, Gothenburg, Sweden, **3** - Sintered Steels – Fatigue and Durability, 397-402 (2013).

[22] A. Ciaś, Science of Sintering **47** (1), 61-69 (2015).
[23] Metalog guide, Struers A/S, 1992.
[24] G. Zapf, G. Hoffmann, K. Dalal , Powder Metall. **18** (35), 214-236 (1975).
[25] F. Benesovsky, R. Kieffer, Berg- u. Huttenmann. Monatsh (8), 145-148 (1960)
[26] K. Mauer H. Grewe, DEW-Techn. Ber, (4), 242 (1968)
[27] A. Šalak, The International Journal of Powder Metallurgy and Powder Technology **16** (4), 369- 379 (1980).
[28] M. Sułowski, A. Ciaś, Arch. Metall. Mater. **49** (1), 55-72 (2004).
[29] M. Tenerowicz-Żaba, M. Sulowski, Science of Sintering **50** (4), 457-466 (2018).
[30] M. Sulowski, Ph. D. Thesis, The structure and mechanical properties of structural sintered Fe-Mn-C steel, AGH UST, Cracow, Poland (2001).
[31] Materials Standard for PM Structural Parts, MPIF,New Jersey (2016).
[32] A. Šalak, M. Selecka, R. Bures, Powder Metallurgy Progress **1** (1), 41-58 (2000).
[33] M. Tenerowicz, M. Sulowski, Arch. Metall. Mater. **62** (4), 2153-2163 (2017).
[34] M. Sułowski, Arch. Metall. Mater. **49** (3), 641-670 (2004).
[35] M. Sułowski, Arch. Metall. Mater. **50** (4), 827-841 (2005).
[36] A. G. Süleyman Tekeli, High Temperature Materials and Processes **32** (2), 119-123 (2013).
[37] M. Sułowski, Arch. Metall. Mater. **52** (4), 617-625 (2007).
[38] M. Sułowski, K. Faryj, Arch. Metall. Mater. **54** (1), 121-127 (2009).
[39] D.J. Bowe, K.R. Berger, J.G. Marsolen, D. Gorg, Int. J. of Powder Met. **31** (1),29-35 (1995)
[40] A. Ciaś, M. Sułowski, Arch. Metall. Mater. **54** (4), 1093-1102 (2009).
[41] M. Sułowski, A. Ciaś, Arch. Metall. Mater. **56** (2), 293-303 (2011).
[42] M. Sułowski, P. Dudek, Arch. Metall. Mater. **53** (3), 827-837 (2008)
[43] V. Petkov, R. Valov¸ M. Witkowska, M. Madej, G. Cempura, M. Sułowski, Arch. Metall. Mater. **64** (4), 1633-1638 (2019).
[44] K. Przybyłowicz, Metaloznawstwo, WNT, Warszawa (1992).
[45] M. Sulowski, Powder Metall. **53** (2), 125-140 (2010).
[46] S.C. Mitchell, A. Cias, Powder Metallurgy Progress **4** (3), 132-142 (2004).
[47] A. Ciaś, S.C. Mitchell, K. Pilch, H. Ciaś, Sułowski, A.S. Wronski, Powder Metall. **46** (2), 165-170 (2003).
[48] T. Pieczonka, M. Suowski, A. Cias, Arch. Metall. Mater. **57** (4), 1001-1009 (2012).
[49] M. Sułowski, A. Ciaś, T. Pieczonka, Arch. Metall. Mater. **59** (2), 575-580 (2014).
[50] M. Sułowski, Arch. Metall. Mater. **59** (4), 1499-1505 (2014).
[51] M. Sułowski, P. Kulecki, A. Radziszewska, Arch. Metall. Mater. **59** (4), 1507-1512 (2014).
[52] M. Sułowski, M. Kabatova, E. Dudrova, Powder Metallurgy Progress **12** (2), 71-83 (2012).
[53] A. Salak, Powder Metallurgy International **18** (4), 266-270 (1986).
[54] W. Schatt, K.-P. Wieters, Powder Metallurgy – Processing and Materials, EPMA, (1997)
[55] M. Sulowski, A. Cias, H. Frydrych, J. Frydrych, I. Olszewska, R. Golen, M. Sowa, Materials Science Forum **534-536** (1), 757-760 (2007).
[56] M. Sulowski, M. Kabatova, E. Dudrova, Powder Metallurgy Progress **11** (1-2), 132-140 (2011).