M. SUŁOWSKI*

SINTERED PM MANGANESE STEELS

SPIEKANE STALE MANGANOWE

High strength structural materials (as-sintered density between 6.8–7.1 Mg/m³ and UTS in the range of 600–1000 MPa are very important group of steels produced by powder metallurgy technique. Due to economic and environmental reasons, manganese steels are very common used for production of sintered gear wheels [1, 2, 3]. The high strength of manganese steels can be achieved as a result of manganese addition and post-sintering heat treatment. To decrease the cost production of these steels, sinter-hardening can be employed [4, 5]. This operation is possible only for groups of alloying steels containing elements given high hardenability, such as nickel and molybdenum.

Nickel has been shown to be a class 3 cancerogenic and allergic element [6]. Thus, due to legislative reasons, most of the investigated steels are nickel-free, in which manganese and/or chromium substitute nickel and expensive molybdenum. Manganese would be an obvious choice for such high strength application if only this element could be protected from oxidation during sintering [3, 7, 8]. If not, during production of PM manganese steels two possible way of oxidation were recognised. Firstly, oxides can be formed because of poor sintering atmosphere dew point. Secondly, iron oxides, which can be reduced by manganese, are the source free oxygen. As a result of this, the reaction between free oxygen and manganese is possible. In a consequence very stable oxides can be created [7], which can be reduced in higher than industrial sintering temperature. The development in furnace construction, allowing for high temperature sintering in oxygen-free atmospheres, caused for increasing in the industrial scale production of sintered steels with addition of elements with high affinity to the oxygen (aluminium, chromium, manganese, titanium).

Nowadays it is widely recognised that the mechanical properties and dimensional changes of the sintered manganese steel depend on grade of the iron powder and sintering temperature variations at different sintering atmosphere dew point level [9]. Also tempering temperature influence the properties of PM manganese structural parts.

Based on the attainable data, which have been published in national and foreign bulletins and presented at international and domestic conferences, author tried to show the main aspects of producing sinter-hardened PM manganese steels.

Keywords: sintered manganese steels, structure and mechanical properties, sinter-hardening, sintering conditions, post-sintering heat treatment, Weibull statistic

Spiekane materiały konstrukcyjne o dużej wytrzymałości na rozciąganie, mieszczącej się w zakresie od 600 MPa do 1000 MPa, i średniej gęstości wynoszącej od 6,8 Mg/m³ do 7,1 Mg/m³, stanowią ważną, wyodrębnioną w normach krajowych i międzynarodowych, grupę materiałów konstrukcyjnych produkowanych techniką metalurgii proszków. Materiały te umożliwiają wytwarzanie części maszyn, łączących w sobie takie cechy jak: względnie duże własności wytrzymałościowe, znikome zanieczyszczenie środowiska naturalnego podczas ich produkcji, stosunkowo małą masę oraz – co najważniejsze – niski koszt wytwarzania. Sprawia to, iż stale spiekane o dużej wytrzymałości stanowią bardzo konkurencyjny materiał w odniesieniu do konwencjonalnych stali konstrukcyjnych i żeliw. Ze stali tych wytwarza się obecnie ostatecznie uformowane, odpowiedzialne, silnie obciążone części maszyn, których typowym przykładem mogą być przekładniowe koła zębate [1, 2, 3]. Duże własności wytrzymałościowe tych stali osiągane są w wyniku obróbki cieplnej polegającej na hartowaniu i niskim odpuszczaniu. W celu obniżenia kosztów produkcji wyrobów ze spiekanych stali konstrukcyjnych, wprowadza się w ostatnich latach obróbkę cieplną, tzw. „sinter-hardening", polegającą na ich hartowaniu bezpośrednio z temperatury spiekania poprzez przyspieszone chłodzenie konwekcyjne [4, 5]. Tego rodzaju obróbka cieplna możliwa jest dzięki zastosowaniu pieców o specjalnej konstrukcji i jedynie w odniesieniu do niektórych gatunków spiekanych stali stopowych, odznaczających się odpowiednio dużą hartownością. Pierwiastkami zapewniającymi dużą hartowność takich stali są z reguły nikiel i molibden. Jednakże, z powodu stwierdzenia silnie kancerogennego oddziaływania proszku niklu na organizm człowieka [6], a także z przyczyn ekonomicznych, czynione są próby zastąpienia niklu innymi pierwiastkami stopowymi, głównie chromem oraz manganem. Niestety wyniki wcześniejszych badań, przeprowadzonych już wiele lat temu, wykluczyły możliwość wytwarzania konstrukcyjnych spiekanych stali manganowych –

* FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, AL. MICKIEWICZA 30, OLAND

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podobnie jak i chromowych – w ówczesnych warunkach przemysłowych. Powodem jest bardzo duże powinowactwo manganu do tlenu oraz wysoka prężność jego par w temperaturze spiekania. Z tego powodu mangan wprowadza się do spieku nie w postaci czystego pierwiastka, lecz zazwyczaj w postaci żelazostopu. Pozwala to znacznie obniżyć koszt produkowanego wyrobu, jednak pojawiają się kłopoty związane z małą prasowalnością mieszanki proszków zawierających żelazomangan [3, 7, 8].

Podczas spiekania konstrukcyjnych stali manganowych występują dwa źródła tlenu. Po pierwsze tlen może dostawać się do materiału bezpośrednio z atmosfery, w której realizowany jest proces spiekania. Aby zapobiec utlenianiu spieku podczas jego produkcji należy stosować atmosfery redukujące o wysokiej czystości oraz odpowiednio niskim punkcie rosy [9]. Drugim źródłem tlenu są tlenki żelaza, które mogą być redukowane przez mangan. Mangan tworzy z tlenem wiele tlenków, z których dwa istnieją w temperaturach wyższych niż 800°C. Są one najbardziej niekorzystne, gdyż ich redukcja nastąpić może w temperaturach wyższych od tradycyjnych temperatur spiekania [7]. Dopiero w ostatnich latach, dzięki postępowi w dziedzinie budowy pieców przemysłowych, pozwalającemu na zastosowanie wyższych temperatur spiekania i atmosfer o wystarczająco małej zawartości tlenu i pary wodnej, stało się możliwe produkowanie również na skalę przemysłową stali z dodatkiem pierwiastków stopowych charakteryzujących się dużym powinowactwem do tlenu, tj. aluminium, chromu, manganu i tytanu.

Na podstawie dostępnych danych literaturowych, opublikowanych w krajowych oraz zagranicznych czasopismach a także w krajowych i zagranicznych materiałach konferencyjnych, w artykule przedstawiono główne aspekty związane z produkcją spiekanych stali manganowych przeznaczonych do obróbki typu sinter-hardening.

Abbreviations

A_{tot}	– elongation (strain to failure)
ATM	– sintering atmosphere
DP	– sintering atmosphere dew point
CR	– cooling rate
E	– Young modulus
HV_{30} surf.	– apparent hardness
HV_{30} app.	– apparent cross-sectional hardness
KC	– impact energy
mag.	– magnification
ND	– not defined
$R_{0,2}$ offset	– 0.2% offset yield strength
ST	– sintering temperature
TRS	– transverse rupture strength
TT	– tempering temperature
UTS	– ultimate tensile strength

1. Introduction

Manganese is potentially an important alloying element in sintered steels. To date it has not been exploited beyond some 0.7 wt.-% due its extremely high affinity to oxygen. Therefore the use of manganese as a major alloying addition requires special precautions such as low dew point of sintering atmosphere, using of semi-closed containers with a special "microclimate" and a high sintering temperature.

In the recent years manganese have been introduced as an alloying element in iron based structural parts on laboratory scale and also for pilot scale production. Nowadays manganese steels are used for production of sintered gear wheels for electric hand-tools.

2. The history of Fe-Mn-C sintered steels

The changes in PM structural steels technology during the last ten years would seem to be compara-

tively small. Major developments have taken place in the sophistication with which manufacturing operations are carried out and in the application of the product. However, there have been major advances in our understanding of the manufacturing processes of the PM manganese steels, and of the mechanisms their sintering [3, 8].

Thus the alloys, although superficially similar to their predecessors of ten years ago, are much more consistent in properties and give substantially better performance. Some recently produced Stackpole PM steels [9, 10] contain manganese, in place of, or in addition to, the more traditional alloying elements. Alloys for ferrous structural PM parts are essentially low to medium carbon low alloy steels containing varying amounts of either or both cooper and nickel, and often, small amount of more expensive molybdenum. This is because these elements have easily reducible oxides and their use has been dictated by production equipment and manufacturing constraints rather than by sound of metallurgical reasoning. The main aim was to substitute nickel, which has been shown to be a class 3 cancerogenic and allergic element [6], by the use of manganese. Manganese would be an obvious choice for such high strength application if only this element could be protected from oxidation during sintering [3]. Cias and co-workers [8, 11, 12, 13] overcame this problem in laboratory and pilot scale. It is now widely recognised that the mechanical properties and dimensional change of the sintered manganese steel depends on grade of the iron powder and sintering temperature variations at different sintering atmosphere dew point level [9]. Manganese PM steels exhibit smaller dimensional scatter than those containing copper. A recently developed alloy, containing 3 wt.-% of Mn, is an alloy which can be processed at link belt furnaces providing that careful control of the oxygen partial pressure of the sintering atmosphere is maintained.

Several notable studies of the effects of manganese on properties of PM steels have been reported. First

works on sintered manganese steels were done by B e - n i o w s k y and K i e f f a r in 1950s. In works published by M a u e r and G r e w e in 1968 and 1971 the mechanical properties and application of these steels were presented.

Outstanding among these, for its elucidation of general principles, is the summarised work of W r o n s - k i and co-workers [14]. For systematic study of the effect of manganese on the mechanical properties of the sintered steel, the works of Z a p f [15] and Š a l a k [16, 17, 18] may be mentioned. Z a p f concluded that manganese have more potent influence on the properties of iron than nickel did [15]. During this researches the effect of manganese donor was investigated. The authors concluded that manganese powder grade does not an influence on the green density of compacts, in the contrary to the mechanism of sintering, where type of manganese donor had a great effect. During these investigations also was shown that addition of manganese in amount of 4–6 wt.-% is optimal to achieve UTS at the 600 MPa level. Also was showed that the best properties were achieved for compacts with addition of 0.6–0.8 wt.-% of carbon. It can be also noticed that atomized iron powder has better compactibility (ISO 3927) than sponge iron powder. It influenced density before sintering of the specimens. It appears that low-carbon ferromanganese powder additions favour higher green density. In most cases, the density involved in tensile testing did not exactly match the density of the transverse rupture specimens. Šalak, on the other hand, stated that oxygen is the most important of all impurities in its effect on mechanical properties of sintered manganese steels. In his papers, the self-cleaning effect of manganese for sintering atmosphere, as combined effect of high affinity of manganese for oxygen, and of high vapour pressure as a basic condition for sintering of manganese steel, was given [16, 17, 18, 19].

3. The present day of Fe-Mn-C sintered steels

During last 60 years sintered manganese steels have been the interest of scientists from all over the world. The main topics of the works have concerned:

- the effect of manganese content and other alloying elements on the mechanical properties of sintered structural parts [6, 10, 12],
- the effect of alloying elements, which in sintering temperatures create liquid phase, on the structure and mechanical properties of sintered manganese steels [10, 20],
- elimination of expensive and cancerogenic nickel and heavy-recycled copper by introducing in sintered steels manganese and chromium causing to increase

the mechanical properties of PM manganese steels [3, 20, 24],
- the porosity problem in these materials [25, 26].

Manganese as an alloying element is added to steel to increase hardenability and mechanical properties. Unfortunately high affinity of manganese to oxygen make some difficulties during production of sintered manganese steels. To protect sintered steels from oxidation, sintering process must be carried out in semi-closed boats or in getter, what was reported in ref. [3].

Research project realised at Powder Metallurgy Laboratory, AGH-UST, Cracow, gave progress in production of sintered manganese steels. Investigations showed that best properties of manganese steels were achieved for the mixture containing sponge iron powder, 3 wt.-% of Mn added in the form of ferromanganese powder and 0.8 wt.-% of graphite powder after sintering in dry hydrogen atmosphere at least 1200°C [3, 20]. The tensile strength for this PM parts about 500 MPa and elongation up to 2% were recorded. In general, the UTS and TRS of the PM manganese steels slightly increases with decreasing dew point of the sintering atmosphere. Decreasing atmosphere sintering dew point increases also impact energy and in some cases apparent surface hardness. The data indicate [20] that the effects of manganese, dew point of the sintering atmosphere and cooling rate on the mechanical properties of the investigated alloys are relatively predictable.

The further improving in mechanical properties was described in [21, 22, 23], where work had concentrated on addition of the ferromanganese to pure iron powder for this purpose. Cooling rates from 2°C/min to 65°C/min were achieved by convective cooling and blowing gas over the specimen [24, 27]. This work has given a comprehensive picture of the structural characteristic and properties of sintered bainitic manganese steels. As the effect of these investigations, it was possible to produce in laboratory scale manganese steel, containing fine pearlite and upper bainite, with TRS up to 1 GPa [4, 5, 20, 28]. The possibility of such high properties was suspect, using the Weibull statistic, reported by C i a s et al. in ref. [22, 23]. During this work, steel with 3 wt.-% of manganese reached the Weibull coefficient m = 17 in the contrary to the steels with addition of 4 wt.-% of manganese for which the Weibull coefficient m = 7 was recorded, as was shown in figure 1.

Cooling rate has a strong effect on the UTS, TRS, impact energy and apparent surface hardness. Decreasing cooling rate to 3.5°C/min in some cases increases mechanical properties by factor up to ~2. Slow cooling rates favoured plasticity, which ceased to be significant for cooling rates above ~ 40°C/min. When slowly cooling is employed, plasticity of the specimens increases,

and tensile elongation is up to 3.8%, as was presented in table 2 [20].

Elongation increased with increasing sintering temperature and density and decreasing dew point of the sintering atmosphere and cooling rate. Both higher manganese concentration and lower sintering temperature increases plasticity PM manganese steels.

The properties of sintered manganese steels are depended on the cooling rate as well as post-sintering heat-treatment. The previous investigation was intended to determine the minimum amounts Mn to give a high strength 0.6–0.8 wt.-% of carbon bainitic/martensitic microstructure over a wide range cooling rates [4, 20, 29, 32, 30] – tables 3–4 and figures 2–4.
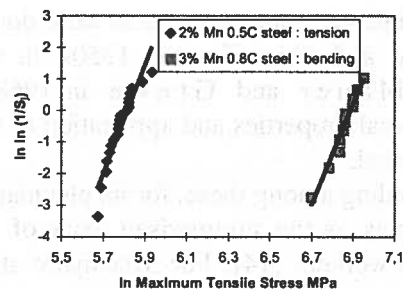

Fig. 1. Weibull plots, where S_j is the survival probability, of maximum tensile stresses of furnace cooled specimens, determined in (a): tension for the 2Mn-0.5C steel and (b): in bending, using the plasticity correction, for the 3Mn-0.8C steel. To be noted is the low scatter in both cases: Weibull moduli of 17 and 16, respectively [8, 14, 22, 23] (Courtesy dr A. Cias)

TABLE 1

Mechanical properties of PM manganese steels sintered in hydrogen atmosphere with a dew point −60°C [4, 5, 20]

CR °/min	ST = 1120°C, DP = −60°C					ST = 1250°C, DP = −60°				
	UTS, MPa	TRS, MPa	HV$_{30}$ surf.	HV$_{30}$ app.	KC, J/cm^2	UTS, MPa	TRS, MPa	HV$_{30}$ surf.	HV$_{30}$ app.	KC, J/cm^2
5	478± 38.56	1272 ±72.61	174± 8.24	224± 9.68	17± 0.02	595± 40.79	1327± 121.19	189± 11.21	254± 36.92	11.5± 4.02
9	506± 33.07	1230± 119.25	183± 11.74	217± 12.82	11± 1.33	614± 58.17	1311± 91.39	189± 15.64	239± 19.93	10± 3.45
16	568± 47.52	1195± 57.87	185± 9.09	248± 22.85	11± 0.46	583± 40.47	1210± 153.84	192± 20.05	265± 47.66	8± 1.17
30	557± 42.09	1124± 69.11	197± 8.68	272± 15.42	8± 1.48	586± 47.89	1193± 200.48	204± 29.9	282± 48.67	9± 4.49
47	559± 49.78	1100± 129.51	202± 10.59	276± 26.64	6± 1.94	521± 56.80	1080± 170.35	218± 29.30	328± 61.28	5± 0.42
55	535± 40.76	954± 155.53	213± 12.49	292± 44.74	5± 0.27	491± 59.94	1087± 129.89	229± 21.95	335± 40.59	5± 0.62
63	498± 49.99	1076± 113.13	197± 12.55	289± 17.42	9± 0.45	507± 87.46	993± 131.43	195± 15.19	276± 47.85	5± 0.25
64	486± 45.52	1003± 109.83	208± 12.70	318± 21.08	6± 1.14	500± 52.67	1109± 167.25	209± 19.29	256± 38.46	4± 0.48
67	475± 100.33	1066± 103.85	206± 16.34	301± 24.18	5± 0.28	458± 81.92	1060± 130.47	210± 21.93	301± 70.23	5± 0.74

TABLE 2

The $R_{0.2}$ yield strength and elongation, A_{tot}, of PM manganese steels sintered in hydrogen atmosphere with a dew point −60°C [4, 5, 20]

CR °/min	ST = 1120°C, DP = −60°C		ST = 1250°C, DP = −60°	
	$R_{0.2}$, MPa	A_{tot}, %	$R_{0.2}$, MPa	A_{tot}, %
5	380±23.30	3.04±0.53	461±29.99	3.80±0.81
9	414±40.55	3.08±0.46	477±48.81	2.87±0.90
16	461±35.02	3.26±0.80	511±51.75	2.42±0.51
30	516±44.24	2.76±0.55	545±31.62	2.22±0.48
47	478±76.67	2.51±0.73	442±97.84	1.96±0.36
55	518±27.18	2.01±0.54	404±90.30	1.62±0.50
63	496±50.04	2.02±0.51	560±45.00	1.82±0.49
64	542±13.12	2.05±0.48	ND	1.75±0.43
67	528±7.50	1.90±0.49	477±91.04	1.46±0.91

Microstructure constituents of Fe-3%Mn-0.5/0.6%C sintered manganese steels. The cooling rate was determined at 800–300°C [27]

CR °/min	Microstructure	
	ST = 1120°C	ST = 1250°C
1.5	Coarse lamellar pearlite	Coarse lamellar pearlite + proeutectoid ferrite
4.5 and 9	Pearlite	Pearlite + proeutectoid ferrite
18	Fine pearlite	Fine pearlite + feathery bainite
30	Feathery bainite + fine pearlite	Acicular bainite + martensite
44	Acicular bainite + martensite + Mn-rich austenite	Acicular bainite + martensite + retained austenite
55, 61, 63, 65	Acicular bainite + martensite + retained austenite	Acicular bainite + martensite + retained austenite

Microhardness (μHV$_{20}$) of the constituents in Fe-3%Mn-0.5/0.6%C sintered manganese steels [27]

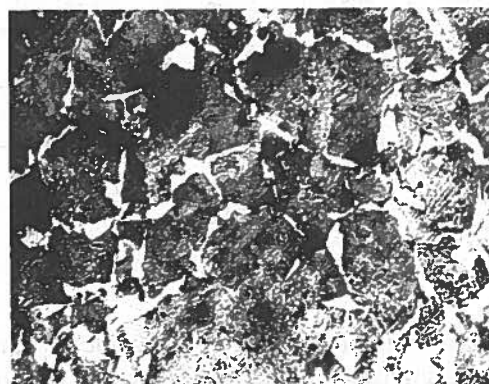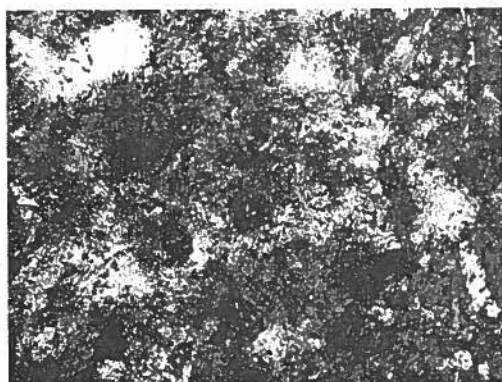| Constituent	Microhardness, μHV$_{20}$
Ferrite	95–160
Pearlite	210–260
Bainite	280–440
Martensite	580–690

Fig. 2. Photomicrograph of PM manganese steels – ATM = 100% H$_2$, DP = –60°C; CR = 5 and 9°C/min, mag. 430x [20, 30]; pearlite, ST = 1120°C (left), pearlite and ferrite – ST = 1250°C (right)
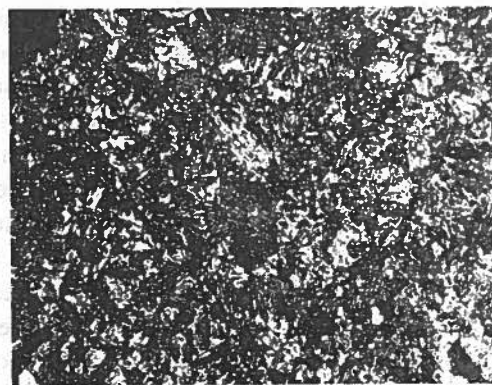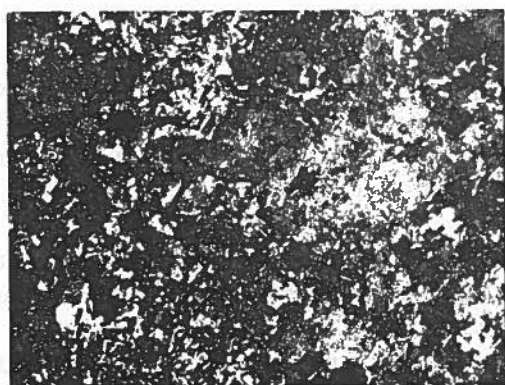

Fig. 3. Photomicrograph of PM manganese steels – ATM = 100% H$_2$, DP = –60°C, mag. 430x [20, 30]; feathery bainite and pearlite, ST = 1120°C, CR = 30°C/min (left) bainite and martensite, ST = 1250°C, CR = 32°C/min (right)
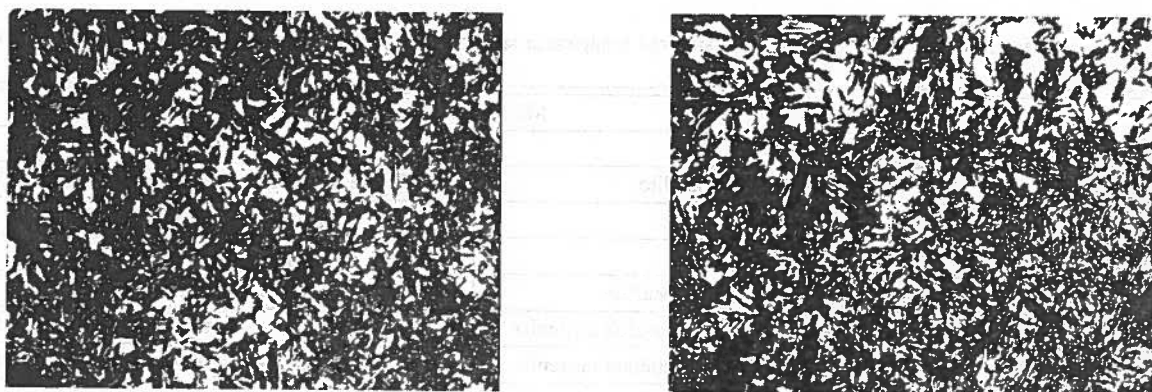
Fig. 4. Photomicrograph of PM manganese steels – ATM = 100% H_2, DP = –60°C, mag. 430x [20, 30]; bainite, martensite and retained austenite, ST = 1120°C, CR > 55°C/min (left), bainite, martensite and retained austenite, ST = 1250°C, CR > 57°C/min (right)

TABLE 5

Mechanical properties of PM manganese steels sintered in hydrogen atmosphere with a dew point –60°C [4, 5, 20]

ST, °C	TT, °C	UTS, MPa	TRS, MPa	HV_{30} surf.	HV_{30} app.	KC, J/cm^2	$R_{0.2}$, MPa	A_{tot}, %
1120	200	740± 33.60	1745± 44.80	250± 15.59	227± 24.68	12± 3.15	411± 22.07	3.91± 0.35
	300	740± 31.22	1507± 63.16	238± 19.06	219± 26.03	10± 0.06	430± 22.07	3.43± 0.36
	400	744± 33.75	1462± 49.60	233± 14.15	216± 18.40	12± 0.83	460± 19.49	3.45± 0.43
1250	200	830± 46.86	1479± 104.66	247± 35.13	278± 33.14	10± 0.98	474± 20.06	3.69± 0.28
	300	798± 40.57	1448± 124.26	252± 24.15	274± 30.92	5± 0.20	472± 19.25	3.03± 0.24
	400	854± 37.19	1755± 86.36	257± 27.93	245± 22.68	16± 0.40	499± 22.48	3.71± 0.32

To produce sintered parts with satisfactory properties, slow cooling rate have to be employed. This process is possible only in laboratory scale, where slow cooling rates below 3°C/min are achieved. Such slow cooling gives opportunity to achieve pearlite and acicular bainite, which decide about high properties of manganese steels. It should be noted, that in industrial condition bainite/martensite structures were more easily produced by continuous cooling (~ 60°C/min), than by isothermal holding. This structure exhibits not only a high hardness, but also tensile strength that approach those of tempered martensite. The lower mechanical properties can be than improved during tempering. Significant improvement in properties was attained as a result of the 200°C stress relief, e.g. 830 MPa tensile strength with 3.7% ductility for the 1250°C sintering temperature. Results were similar for the 400°C temper and there was an indication of temper embrittlement at 300°C, more severe for the specimens sintered at 1250°C, as was shown in table 5 [20, 24].

C i a s, S u l o w s k i, W r o n s k i, S t o y t c h e v and M i t c h e l l [20, 24, 27, 28, 30] have shown that in Fe-3%Mn-(0.5Mo)-(0.6-0.8)%C sintered alloys two microstructures of identical strength, one consisting of bainite and the other of tempered martensite, have distinctly different impact strength. They have shown, that the major part of strength of tempered martensite originates from the smaller ferritic grain size (inherited from the fineness of the martensitic needles) and the uniform dispersion of small carbide particles. However, although the properties of 0.6–0.8 wt.-% of carbon, 3 wt.–% of manganese, sinter-hardened steels have been described in some detail [8, 12], there has been no attempt to determine systematically the effect of tempering temperature.

For sinter-hardened and tempered bainite/tempered martensite manganese PM steels, tempering transformations inducted plasticity has been examined as a means of obtaining a better balance of strength and ductility at more economically viable cost levels. It is now recognised that a not significant amount of manganese, non-expansive alloying element, which is required plus the tight process control to enable the phenomenon to be used in a cost-effective manner makes it possible

to introduce PM manganese steels into practical production. Treatments (cooling rate 10-15°C/min) which will be compatible with a continuous sintering industrial line are designed to produce bainite in Fe-3%Mn-0.8%C steel. The amounts of bainite and martensite present in steels are increased significantly with the higher cooling rate thus resulting in increasing apparent cross-section hardness values. On the other hand the microstructure of Mn steels contains a significant portion of pearlite in the slow cooled (1.5–4.5°C/min) state.

The austenitic grain size is another factor that affects hardenability. In high temperature sinter-hardening, increasing the austenitic grain size has been reported to have an appreciable effect in retarding the ferrite and pearlite reaction [30]. These results suggest that steels high temperature sinter-hardened to produce large austenitic grains would have a greater chance to transform to bainite/martensite.

It is also well-accepted fact that the strength of a manufactured specimen (and part) is a variable quantity that should be modelled as a random variable. This fact forms the basis for all of reliability modelling. A second source of variability may also have to be taken into account. This is uncertainly about the actual environmental stress to be encountered should be modelled as random. When ascertaining the reliability of specimen or the viability of a material, it is also necessary to take into account the stress conditions of the operating environment. The stress-strength reliability model is an integral part of many risk analyses. At the component level, for instance, it may be necessary to make an assessment of the reliability of a structural part operated value in a mechanical device. The application of the stress-strength model has one dominant feature. Little or no data are available on either the critical stress or even on the strength of component. Prior to using a probability model to represent the population underlying data, it is important to test adequacy of the model. One way to this is by a goodness-of-fit test. However one must make an initial selection of models to be tested. Several avenues are available for an initial screening of the data. One could construct histograms, frequency polygons or more sophisticated non-parametric density estimates. After one has selected a model to be tested further, an initial screening of the model could be done by a goodness-of-fit parallel test presented above. This classical test is an almost universal goodness-of-fit test. It requires moderate to large sample sizes [31].

TABLE 6

Properties data for as-sintered Fe-3%Mn-(0-1)%Sn-0.8%C specimens. The alloys were sintered 1 hour at temperature 1150 and 1180°C in H_2 atmosphere of −60°C dew point − CR = 60°C/min [32]

Sn, wt. %	ST = 1150°C, DP = −60°C					ST = 1180°C, DP = −60°				
	UTS, MPa	TRS, MPa	HV_{30} app.	$R_{0.2}$, MPa	A_{tot}, %	UTS, MPa	TRS, MPa	HV_{30} app.	$R_{0.2}$, MPa	A_{tot} %
0	540± 26.55	997 ±41.16	167± 6.10	220± 5.76	1.83± 0.07	480± 65.05	1002± 46.85	153± 13.85	220± 17.07	1.72± 0.38
0.1	506± 29.68	1012± 45.59	171± 8.92	244± 13.04	1.54± 0.02	494± 62.53	1037± 63.45	172± 5.30	225± 6.09	1.53± 0.20
0.15	547± 27.08	974± 41.94	178± 27.70	233± 5.67	1.88± 0.12	524± 32.03	1008± 30.32	165± 2.04	229± 8.57	1.85± 0.14
0.20	489± 18.74	965± 18.61	178± 9.85	255± 2.27	1.89± 0.25	467± 53.83	975± 60.43	191± 16.75	241± 6.28	1.27± 0.40
0.25	477± 41.86	1070± 68.52	179± 18.21	248± 12.52	1.64± 0.27	472± 43.12	1006± 87.37	173± 10.27	220± 53.76	1.58± 0.38
0.30	497± 23.61	966± 47.99	169± 6.23	235± 2.14	1.60± 0.28	478± 39.46	898± 93.44	175± 6.57	246± 3.16	1.40± 0.27
0.35	475± 32.22	841± 36.90	160± 9.07	235± 0.94	1.39± 0.43	494± 18.81	944± 58.43	180± 3.33	229± 7.73	1.99± 0.18
0.50	463± 104.05	919± 38.87	182± 1.70	231± 1.35	1.28± 0.57	422± 55.80	916± 39.13	194± 11.62	244± 18.60	1.12± 0.51
0.75	275± 55.73	896± 41.47	211± 20.63	215± 0.00	0.82± 0.00	257± 75.69	866± 67.11	197± 12.02	258± 0.00	0.45± 0.00
1.00	237± 72.30	847± 54.22	192± 2.32	218± 48.11	0.89± 0.69	254± 46.14	845± 21.12	195± 2.61	207± 33.45	0.37± 0.09

TABLE 7

Mean values of the Young's modulus, E, yield strength, $R_{0.2}$, tensile strength, TRS and elongation, A, for the 10 batches of specimens sintered in dry hydrogen, nitrogen and combinations thereof [33]

Sintering conditions	E, GPa	$R_{0.2}$, MPa	TRS, MPa	A, %
1120°C – H_2 only	114±5	386±23	633±59	1.8±0.4
1120°C – 75%H_2 – 25%N2	115±6	400±24	639±39	1.8±0.3
1120°C – 25%H_2 – 75%N_2	120±5	420±13	648±35	1.8±0.3
1120°C – 5%H_2 – 95%N_2	122±4	421±17	654±32	1.8±0.2
1120°C – N_2 only	117±6	410±12	652±30	1.9±0.2
1250°C – H_2 only	117±6	426±26	724±39	1.6±0.1
1250°C – 75%H_2 – 25%N_2	117±4	443±16	741±37	1.7±0.2
1250°C – 25%H_2 – 75%N_2	120±4	459±12	780±28	1.8±0.2
1250°C – 5%H_2 – 95%N_2	118±5	451±21	728±74	1.6±0.3
1250°C – N_2 only	122±5	464±22	776±33	2.0±0.2

TABLE 8

Mechanical properties of PM manganese steels sintered in dry hydrogen, nitrogen and combinations thereof – tempering temperature 200°C [20]

H_2, %	ST = 1120°C, DP = –60°C, CR = 67°/min					ST = 1250°C, DP = –60°, CR = 64°/min				
	UTS, MPa	TRS, MPa	HV$_{30}$ app.	HV$_{30}$ surf.	KC, J/cm^2	UTS, MPa	TRS, MPa	HV$_{30}$ app.	HV$_{30}$ surf.	KC, J/cm^2
100	642± 44.21	1279± 92.80	196± 15.87	236± 25.01	4.68± 0.00	717± 37.84	1296± 87.42	212± 12.68	315± 64.39	5.04± 0.00
75	640± 36.43	1291± 92.71	195± 14.67	247± 34.57	5.09± 0.00	749± 32.07	1343± 140.99	212± 26.23	295± 59.02	13.3± 0.00
25	650± 36.60	1299± 66.33	201± 19.43	226± 31.24	7.44± 0.00	778± 28.59	1411± 112.92	222± 12.51	298± 58.19	10.83± ND
5	657± 30.18	1234± 115.83	197± 6.72	186± 32.93	7.27± 0.00	725± 68.81	1420± 114.34	221± 10.10	266± 44.20	12.45± 0.00
0	655± 29.24	1259± 100.13	212± 3.28	202± 24.81	14.31± 0.00	776± 35.09	1458± 84.26	228± 16.33	260± 32.32	13.23± 0.00

TABLE 9

The $R_{0.2}$ yield strength and elongation, A_{tot}, of PM manganese steels sintered in dry hydrogen, nitrogen and combinations thereof – tempering temperature 200°C [20]

H_2, %	ST = 1120°C, DP = –60°C, CR = 67°/min		ST = 1250°C, DP = –60°, CR = 64°/min	
	$R_{0.2}$, MPa	A_{tot}, %	$R_{0.2}$, MPa	A_{tot}, %
100	386± 21.62	1.87± 0.27	426± 24.44	1.60± 0.14
75	400± 22.80	1.79± 0.27	443± 15.85	1.71± 0.23
25	420± 12.54	1.78± 0.28	459± 11.58	1.82± 0.16
5	421± 14.91	1.82± 0.17	451± 20.10	1.67± 0.25
0	410± 10.59	1.93± 0.23	464± 20.86	2.00± 0.24

In iron-manganese-tin-carbon alloys the manganese-alloyed zones grow into the iron particles and bainitic/martensitic rims include most of the particles [32]. Small amounts of ferrite could be seen in the microstructures of specimens only when no tin addition was used. In the case of manganese steels contained tin and graphite powders and sintered at 1150 and 1180°C. it was evident that the distribution of manga-

nese is less inhomogeneous. The effect of sintering temperature was only moderate. It is suggested that successful industrial sintering at 1150°C may be achieved. The mechanical properties (hardness. transverse rupture strength and tensile strength) show the effect of tin addition and the optimal tin concentration is 0.15–0.25 wt.-%. Dimensional changes on sintering were acceptable, generally less than 1% and densities were in the range 6.8–7.0 g/cm^3 – table 6.

On the other hand most of scientists till nowadays thought it is impossible to sinter manganese steels in, other than hydrogen, atmospheres. As was shown in [20, 33], sintering in cheaper than pure hydrogen, low- or free-hydrogen atmospheres can be also used for production of sintered manganese steels. The mechanical properties on the same level or higher as in steels sintered in hydrogen were recorded, what was shown in tables 7–9. It was caused by the set of chemical reactions mentioned in ref. [33], which exist even during sintering in nitrogen atmosphere and are responsible for oxide reduction.

4. Conclusions

Accelerated cooling technique for laboratory sintering furnace has been developed which permits larger manganese steel part to be sinter-hardened. Sintered manganese steels with sufficient hardenability develop microstructures containing significant percentage of manganese in the as sintered conditions. The Fe-Mn-C alloys differ from the classical eutectoid iron-carbon system regarding transformation to "pearlitic" and "martensitic" structure. Pearlitic transformation is slower in this alloy, and manganese austenite is more stable with respect to transformation to martensite. Convective cooling gives much higher hardness – the structure of sintered material is bainite/martensite matrix, which contains some retained austenite. This materials show also a very heterogeneous structure consisting of martensite, coarse and fine bainite, retained austenite and sometimes ferritic cores of the iron powder particles. To make the structure less heterogeneous three tempering temperatures have to be employed. Also nowadays it is possible to produce sintered manganese steels without decreasing their properties in low- or free-hydrogen atmospheres.

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