DOI: 10.2478/v10172-011-0033-9

Volume 56 2011

M. SUŁOWSKI*, A. CIAŚ*

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Cr-Mn STRUCTURAL PM STEELS

MIKROSTRUKTURA I WŁASNOŚCI MECHANICZNE SPIEKANYCH, KONSTRUKCYJNYCH STALI CHROMOWO-MANGANOWYCH

The effects of chemical composition, sintering atmosphere and cooling rate on density, microstructure and mechanical properties of Fe-3%Mn-(Cr)-(Mo)-0.3%C PM steels are described. Pre-alloyed Astaloy CrM and Astaloy CrL, ferromanganese and graphite powders were used as the starting materials. After pressing in rigid dies the compacts were sintered at 1120 and 1250°C for 60 minutes atmospheres with different H₂/N₂ ratios and cooled either at 1.4°Cmin⁻¹ (with the furnace) or 65°Cmin⁻¹ (convective cooling). The convective cooled specimens were subsequently tempered at 200°C for 60 and 240 minutes. All specimens were tested for tensile strength (UTS), elongation (A), offset yield strength (R_{0.2}), TRS, impact toughness and apparent surface hardness (HV 30). After mechanical tests the microstructure of the Fe-Mn-Cr-Mo-C PM steels was studied by optical microscopy. It has been found that by sintering in inexpensive and safe nitrogen-rich atmospheres it is possible to achieve properties similar to those shown by specimens sintered in a hydrogen-rich atmosphere.

Keywords: PM Cr-Mn steels, mechanical properties, sintering atmosphere, cooling rate, sinter-hardening

W pracy przedstawiono wpływ składu chemicznego mieszanki proszków, a także rodzaju atmosfery oraz szybkości chłodzenia na gęstość, mikrostrukturę oraz własności mechaniczne spiekanych stali konstrukcyjnych Fe-3%Mn-(Cr)-(Mo)-0.3%C. Do badań wykorzystane zostały wstępnie stopowane, komercyjne proszki żelaza Astaloy CrL i Astaloy CrM, produkcji szwedzkiej firmy Höganäs oraz niskowęglowy proszek żelazomanganu i proszek grafitu. Prasowanie mieszanek proszków o żądanym składzie chemicznym realizowano w stalowych matrycach, wykonując wypraski prostopadłościenne o wymiarach 5×10×55 mm oraz wytrzymałościowe (zgodne z PN-EN ISO 2740). Spiekanie kształtek odbywało się w temperaturze 1120 i 1250°C w czasie 60 minut, w atmosferze o różnej zawartości wodoru i azotu. Chłodzenie spieków prowadzono z szybkością 1,4°C/min (z piecem) lub 65°C/min (konwekcyjnie w chłodnicy pieca). Spieki chłodzone z szybkością 65°C/min poddane zostały odpuszczaniu w temperaturze 200°C w czasie 60 i 240 minut. Spieczone kształtki poddano statycznej próbie rozciągania oraz próbie trójpunktowego zginania; przeprowadzone również zostały badania udarności oraz pomiary twardości. Badania mikrostruktury spiekanych stali prowadzono z wykorzystaniem mikroskopii świetlnej. W toku prowadzonych badań wykazano, że spiekanie kształtek w taniej i bezpiecznej atmosferze azotu (lub w atmosferach bogatych w azot) pozwala uzyskać zadowalające własności mechaniczne spieków, porównywalne z własnościami tych stali, wytwarzanych poprzez spiekanie w atmosferze wodoru.

1. Introduction

The potential of Mn and Cr as alloying elements, reflected in their widespread use in wrought medium-to-high strength steels, is to be realised in powder metallurgy. An interesting development in the processing of PM steels is the addition of Mn to Fe-Cr-0.5%C steels sintered at above 1250°C [1]. The mechanical properties of these steels were largely determined by the microstructure, so it is important to know how alloying elements affect hardenability and microstructural features. Obviously the effect of Mn on Cr

steel strength is due to the combination of Mn, Cr, N and C present in the sintering atmosphere [2]. For Astaloy CrL and Astaloy CrM containing 1.5 and 3% Cr endogas is too wet for their processing. This group of steels has to be specially treated during sintering because of high affinity of Mn and Cr for oxygen. Manganese intensifies the detrimental effect of oxygen on mechanical properties of PM Cr steels. Cracked ammonia, traditionally used as a sintering atmosphere for low-alloy steel components, is being substituted by N₂/H₂ mixtures containing up to 10% H₂. To process Astaloy CrM industrially, however, methane is injected into the N₂/H₂ atmosphere.

^{*} AGH-UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, DEPARTMENT OF PHYSICAL AND POWDER METALLURGY, 30-059 KRAKÓW, 30 MICKIEWICZA AV., POLAND



It is known that chromium causes a large increase in the solubility of nitrogen in steel.

Hardened microstructures resulting in an optimum combination of strength and ductility can be formed during the sinter-hardening cycle by using furnaces which allow higher cooling rates and subsequent tempering at ~200°C. As a result, higher amounts of bainitic/martensitic structures can be expected. This was illustrated for Fe-3%Mn-(Mo)-0.6%C alloys [2-4]. Very slow furnace cooling (1.4°Cmin⁻¹) was found to favour plasticity [5]. Significant improvements in the properties were observed in specimens cooled at 65°Cmin⁻¹ and subsequently tempered at 200°C. The as-sintered specimens showed low impact toughness but tempering at 200°C resulted in precipitation of the ε -carbide in low-carbon martensite, which lowers internal stresses [6]. Some PM steels are used in the fully bainitic/martensitic condition [7]. However, some thermal treatments, including rapid cooling from the sintering temperature, often result in embrittlement. Cias et al [8] have demonstrated that the problems of successful PM exploitation of steels containing ~3% Mn are associated with elimination of oxide networks present in such alloys by sintering in reducing atmospheres having dew points of -55°C or -40°C at 1120°C and 1200°C, respectively. It has also been shown [9-10], that for successful processing of Mn containing steels it is essential that the dew point of the furnace N_2/H_2 atmosphere must be strictly controlled and as low as possible.

Only control of the "local microclimate" ensured by use of semi-closed container, or getter, minimised interactions with the flowing atmosphere. CO generated within a PM component should prove to be a more efficient reducing agent than pure dry hydrogen at above 900°C and high temperature carbothermic sintering at 1250-1280°C has been found important to produce the best combination of strength and ductility [11].

The aim of the present study was to establish an economical route of producing low-alloy nitrogen-free structural steels, and second, to substitute Ni, classified as class 3 carcinogen and allergic element [12], with Mn.

2. Experimental methods, materials and procedures

Pre-alloyed Höganäs Astaloy CrL and Höganäs Astaloy CrM were used as the base powders. 3% of manganese, in the form of low-carbon (1.3% C) ferromanganese (77% Mn) powder, and 0.3% ultra fine graphite powder were added to the base powders in order to prepare two mixtures Fe-3%Mn-1.5%Cr-0.2%Mo-0.3%C or Fe-3%Mn-3%Cr-0.5%Mo-0.3%C (based on pre-alloyed Astaloy CrL and Astaloy CrM, respectively) by intermingling the components in a Turbula mixer for 30 minutes. The mixed powders were then compacted in steel dies with zinc stearate lubricated walls. Two types of compacts with approximately the same density were prepared: 5×10×55 mm TRS specimens and ISO 2740 dog-bone tensile test bars. The green (d_1) and as-sintered (d₂) densities of the compacts are summarised in Table 1. Isothermal sintering was carried out in dry (30 ppm moisture) atmospheres with different H₂ to N₂ ratio (Table 2) in a laboratory horizontal tube furnace at 1120 and 1250°C for 60 minutes, employing slow (1.4°Cmin⁻¹) and convective (65°Cmin⁻¹) cooling.

Green and as-sintered densities of Fe-Mn-Cr-Mo-C PM steels (mean values)

As-sintered density As-sintered density Green density Green density ISO 2740 bars rectangular 5×10×55 mm bars Chemical composition 1120°C 1250°C 1120°C 1250°C d₂, g/cm³ d_2 , g/cm³ d_1 , g/cm³ d_1 , g/cm³ Fe+1.5%Cr+0.2%Mo+3%Mn+0.3%C 6.92 6.91 6.91 7.14 7.08 7.18 Fe+3%Cr+0.5%Mo+3%Mn+0.3%C 7.06 7.00 7.09 6.86 6.84 6.88

TABLE 2

TABLE 1

Sintering atmospheres

Designation of atmosphere	Chemical compositions
A0	100%H ₂
A1	75%H ₂ -25%N ₂
A2	25%H ₂ -75%N ₂
A3	5%H ₂ -95%N ₂
A4	100%N ₂

TABLE 3



For each chemical composition of steels, 5 batches of specimens were sintered in each (A0-A4) atmosphere and tempered at 200°C for 60 and 240 min. To improve the local dew point of microatmosphere and to minimise the loss of manganese due to volatilisation, sintering was carried out in a semi-closed stainless steel container. The mechanical properties of investigated steels are given in Tables 3-5.

3. Results

The physical and mechanical properties of Fe-Mn-Mo-Cr-C PM steels are summarised in Tables 1,3 and 4. Green and as-sintered densities were calculated using geometrical method. The results were then verified using Archimedes' method (Table 1).

As was presented in Table 3, for higher Cr and Mo concentration, high temperature sintering in nitrogen has to be employed to improve strength properties. Recorded values for UTS, elongation and TRS after sin-

tering at 1250°C were higher than that after low temperature process. These values correspond well to the bainitic/martensitic structure of PM steels. What is more, there is no evident percentage differences between sintering in H₂-rich and pure N₂ atmosphere. For lower Cr and Mo concentration, slightly better properties were recorded after sintering in hydrogen-rich than in nitrogen atmosphere, irrespective to the sintering temperature. Young's modulus evaluated by the supersonic method along the sample was in the range of 144-151 GPa. When we look at plasticity and hardness of Mn-Cr-Mo PM steels (Table 3), the same tendency as in strength properties can be observed. It can be also pointed out relatively high elongation - up to 2.5%, which corresponds well with the impact toughness. The microstructure of slow (1.4°Cmin⁻¹) cooled, not tempered PM steels are shown in Figs 1-4. In Table 4 and 5 the mechanical properties of the investigated steels after tempering at 200°C for 0, 60 and 240 minutes were summarised. The microstructure of convective (65°Cmin⁻¹) cooled and tempered PM steels are shown in Figs 5-10.

As-sintered properties of Fe-Mn-Cr-Mo-C PM steels cooled at 1.4°C/min (mean values)

Chemical composition	Sinter	ing temperature,°C, and atmosphere	UTS, MPa	R _{0.2} , MPa	A, %	TRS, MPa	Toughness, Jcm ⁻²	HV30
		A0	662	408	1.8	1460	5.61	231
	1120	A1	512	455	1.3	872	4.1	190
Mo		A2	438	361	0.9	1024	2.7	207
Fe+1.5%Cr+0.2%Mo +3%Mn+0.3%C		A3	400	342	0.8	814	2.8	247
Cr.+C		A4	374	285	0.7	909	2.6	229
1.5% 3%N	1250	A0	629	453	1.5	1514	11.2	222
Не+ +		A1	602	440	1.6	1226	5.7	260
		A2	510	462	1.1	1214	5.8	249
		A3	456	484	0.8	1208	3.9	235
		A4	466	440	1.2	970	3.9	225
	1120	A0	598	541	0.9	1104	5.1	322
		A1	584	498	1.1	969	4.0	255
t o		A2	532	451	1.1	1048	3.9	302
5%N 3%C		A3	515	386	1.0	972	3.5	341
!r+0.; n+0.		A4	495	479	1.0	975	3.9	353
Fe+3%Cr+0.5%Mo+ 3%Mn+0.3%C	1250	A0	774	546	1.8	1425	7.7	254
Fe+.		A1	816	587	2.5	1469	7.2	326
		A2	672	569	1.5	1145	4.7	345
		A3	572	526	1.1	1026	4.8	351
		A4	670	-	2.0	1056	3.7	362

It was found that the steel microstructure strongly depends on the cooling rate after sintering. Bainitic or bainitic/martensitic structure was formed during cooling at 30° Cmin⁻¹ and 20° Cmin⁻¹ after sintering at 1120 and 1250° C, respectively. In general, the bainitic structure is relatively acicular and much finer than the pearlitic one. This accounts for the improved bending and tensile properties. In investigated steels bainite consists of an aggregate of acicular ferrite and carbides. Its morphology changes progressively with the transformation temperature, i.e. the grain size and acicularity of the structure increases as the temperature decreases. The upper bainite comprises larger ferrite plates bounded by Fe₃C precipitates that form directly from the austenite.

It has been shown [1, 10, 13, 14] that the structures form in situations that didn't correspond to the accepted classical definition. These structures consisted of fine bainite and Mn-rich retained austenite zones, partly transformed into martensite, that do not necessarily contain carbides. When long austenitic-martensitic plates extend across the grains, the impact strength sharply decreases. Finally, a spectacular strength increase along with a marked decrease in impact strength is observed in most specimens when a certain amount of acicular martensite is formed inside the acicular-bainitic regions at the end of the bainitic transformation. Continuous cooling results in a mixture of upper and lower bainitic structures unless the transformation is substantially suppressed by the prior occurrence of the equilibrium, pearlitic transformation.

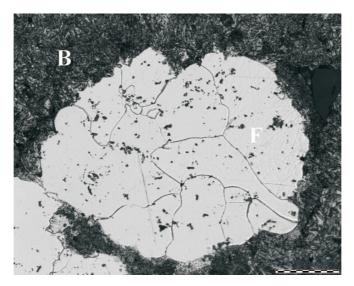


Fig. 1. Micrograph of Astaloy CrL-based PM steel sintered at 1120°C in H₂; ferrite island (F) in bainite (B) matrix, mag. 500x

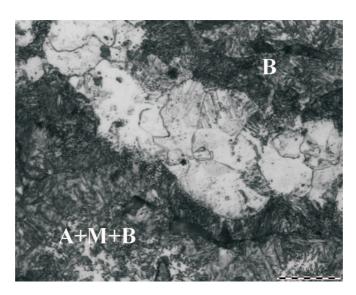


Fig. 2. Micrograph of Astaloy CrL-based PM steel sintered at 1120° C in N_2 ; austenite (A) / martensite (M) / bainite (B) (A+M+B), mostly bainite (B); mag. 500x

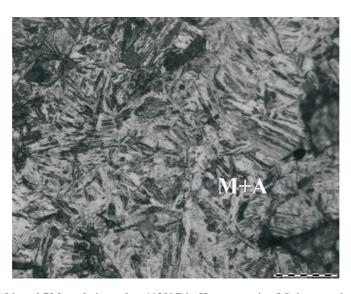


Fig. 3. Micrograph of Astaloy CrM-based PM steel sintered at 1120°C in H₂; martensite (M) in austenite (A) matrix; mag. 500x

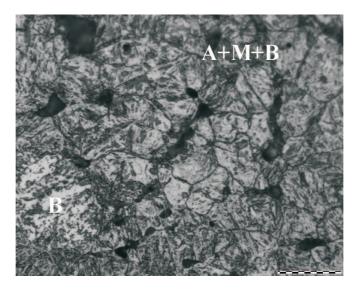


Fig. 4. Micrograph of Astaloy CrM-based PM steel sintered at 1120° C in N_2 ; austenite (A) / martensite (M) / bainite (B) (A+M+B), bainitic (B) islands; mag. 500x

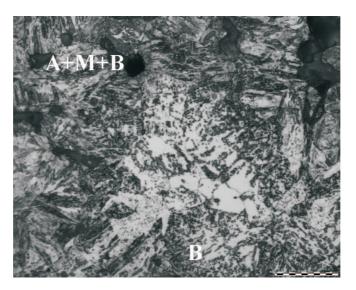


Fig. 5. Micrograph of Astaloy CrL-based PM steel sintered at 1120° C in H_2 , not tempered; austenite (A) / martensite (M) / upper bainite (B) islands; mag. 500x



TABLE 4 Mechanical properties of Fe-Mn-Cr-Mo-C PM steels sintered at 1120°C, rapidly cooled at 65°Cmin⁻¹ and tempered at 200°C

Chemical composition / sintering atmosphere / tempering time, min			UTS, MPa	R _{0.2} , MPa	A, %	TRS, MPa	Toughness, Jcm ⁻²	HV30
Fe-1.5%Cr+0.2%Mo+3%Mn+0.3%C		0	545	_	1.0	1171	6.0	198
	A0	60	554	481	0.8	1216	3.4	245
		240	625	553	0.6	1163	5.2	263
[n+0]		0	514	507	0.8	825	4.1	222
%W	A1	60	439	-	0.6	1017	3.0	262
1o+3		240	662	457	1.1	1045	3.9	210
.2%N		0	634	517	1.2	1003	4.1	342
\r+0.	A2	60	662	608	1.0	1049	3.6	318
5%C		240	608	554	0.9	1018	7.0	280
Fe-1.		0	654	498	1.1	805	4.8	317
	A3	60	542	481	0.8	1020	3.0	284
		240	506	405	0.7	912	2.5	278
		0	495	450	0.8	765	4.3	315
	A4	60	541	481	0.8	1191	3.4	274
		240	544	508	0.8	1082	3.4	298
		0	_	-	-	1041	4.6	389
	A0	60	439	357	0.6	1195	5.8	305
2%C		240	687	635	1.2	1096	5.5	291
+0.3		0	447	-	0.7	702	3.0	206
6Mn	A1	60	563	-	0.8	1030	3.3	268
0+3¢		240	535	474	0.8	1230	3.5	310
%W(0	642	537	1.1	689	5.5	400
+0.5	A2	60	645	560	1.1	1105	5.0	317
%Cr		240	575	517	0.9	1035	4.0	309
Fe+3%Cr+0.5%Mo+3%Mn+0.3%C		0	416	_	0.5	828	4.1	372
	A3	60	648	537	1.7	982	3.3	323
		240	621	577	2.0	941	3.2	307
		0	595	492	1.9	399	2.5	395
	A4	60	706	535	2.5	855	4.1	320
		240	700	587	2.5	1131	4.1	319



TABLE 5 Mechanical properties of Fe-Mn-Cr-Mo-C PM steels sintered at 1250° C, rapidly cooled at 65° Cmin⁻¹ and tempered at 200° C

		composition / sintering re / tempering time, min	UTS, MPa	R _{0.2} , MPa	A, %	TRS, MPa	Toughness, Jcm ⁻²	HV30
		0	573	410	1.1	1354	14.0	252
	A0	60	604	474	1.2	1613	15.2	222
Fe-1.5%Cr+0.2%Mo+3%Mn+0.3%C		240	630	543	1.2	1412	14.1	239
[n+0.		0	594	447	1.3	1214	11.4	253
1%8	A1	60	682	475	1.5	1549	10.9	244
40+3		240	638	506	1.4	1358	10.7	251
2%1		0	622	505	1.2	1530	7.7	220
7r+0	A2	60	753	537	1.6	1348	6.5	278
5%(240	791	557	1.7	1530	9.2	282
Fe-1.		0	799	472	1.8	1519	5.2	296
	A3	60	785	535	1.7	1407	6.0	273
		240	669	565	1.2	1169	6.3	268
	A4	0	822	554	2.2	1428	10.4	281
		60	829	554	2.0	1469	5.8	272
		240	813	596	1.7	1702	15.3	262
	A0	0	858	563	2.3	1349	7.9	314
		60	811	594	1.8	1543	6.6	302
%C		240	813	598	1.7	1463	5.8	282
1+0.3	A1	0	781	521	1.6	1501	8.2	306
%Mn		60	752	632	1.3	1665	8.1	313
0+36		240	808	601	1.7	1428	6.4	296
%W	A2	0	886	573	2.3	1610	7.9	331
:+0.5		60	905	613	2.3	1695	6.9	304
%C		240	811	576	1.7	1598	10.1	329
Fe+3%Cr+0.5%Mo+3%Mn+0.3%C	A3	0	901	604	2.2	1572	13.0	334
		60	872	615	2.2	1610	8.9	319
		240	925	595	2.8	1705	8.4	338
		0	802	583	1.7	1675	14.1	328
	A4	60	954	562	2.8	1658	10.7	315
		240	965	584	2.8	1527	8.0	327

Chemical analysis using Leco instruments was employed to check the carbon and oxygen content of the investigated steels. As shown in Table 6, decarburisation was observed. The higher carbon loss, of 0.11%, was recorded for CrM samples sintered at 1250° C in A3 atmosphere with H_2/N_2 ratio 3:1.

As shown in Figs 1-10, specimens with lower Cr and Mo content, sintered at 1120°C, show a bainitic/martensitic structure, whereas in those containing more Cr and Mo, martensitic/austenitic structures are mainly observed. After sintering at 1250°C, the structure consists mainly of martensite and bainite regions with small amount of austenite.



Oxygen and carbon content of PM Fe-Mn-Cr-Mo-C steels

TABLE 6

Sintering temperature, °C and atmosphere		Fe+1.5%C	r+0.2%Mo+3%Mn+0.3%C	Fe+3%Cr+0.5%Mo+3%Mn+0.3%C		
Sinter	Sintering temperature, 'C and atmosphere'		C, wt% O ₂ , wt%		O ₂ , wt%	
	A0	0.287	0.587	0.303	0.507	
1120	A1	0.266	0.331	0.277	0.310	
	A3	0.289	0.460	0.304	0.390	
	A4	0.274	0.338	0.276	0.333	
	A0	0.221	0.252	0.218	0.343	
1250	A1	0.208	0.140	0.221	0.161	
	A3	0.190	0.157	0.228	0.290	
	A4	0.191	0.165	0.214	0.280	

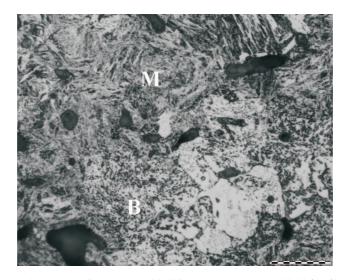


Fig. 6. Micrograph of Astaloy CrL-based PM steel sintered at 1120° C in H_2 , tempered at 200° C for 60 min; bainite (B) in martensite (M) matrix; mag. 500x

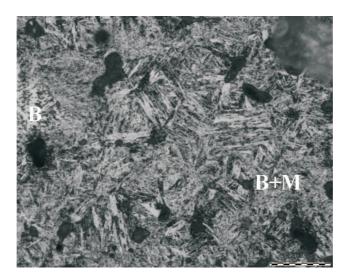


Fig. 7. Micrograph of Astaloy CrL-based PM steel sintered at 1120° C in H_2 , tempered at 200° C for 240 min; bainite (B) / martensite (M) (B+M); mag. 500x

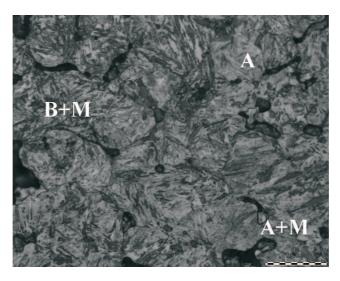


Fig. 8. Micrograph of Astaloy CrM-based PM steel sintered at 1120° C in N_2 , not tempered; martensite (M), austenite (A) and acicular bainite (B); mag. 500x

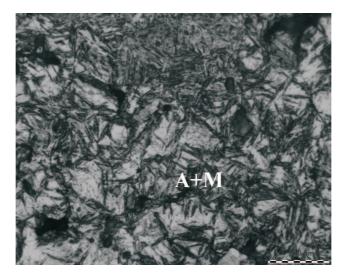


Fig. 9. Micrograph of Astaloy CrM-based PM steel sintered at 1120° C in N_2 , tempered at 200° C for 60 min; austenite (A) + martensite (M) (A+M); mag. 500x

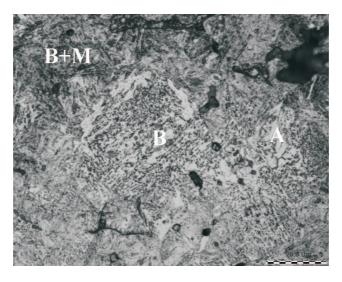


Fig. 10. Micrograph of Astaloy CrM-based PM steel sintered at 1120° C in N_2 , tempered at 200° C for 240 min; bainite (B), austenite (A), martensite (M); mag. 500x



4. Discussion and conclusions

The investigated alloys belong to the group of low alloyed sinter-hardened medium-to-high strength steels, which are used for structural parts in ferrous powder metallurgy and with success substitute traditional, expensive PM steels. The tensile and yield strengths of investigated steels were in excess of 850 MPa and 550 MPa, respectively. The aim of the work was to develop, by single compaction processing, PM steels with properties typical of double pressed sintered steels.

Sinter-hardening steel is usually produced in a sintering furnace with a gas rapid cooling function. If the hardened structure can be obtained at a normal cooling rate (~ 10°Cmin⁻¹), a sintering furnace with a conventional cooling zone can be used and larger economic benefit will be brought. In these investigations, by selecting and adding the optimum quantities of alloying elements that improve hardenability, a martensitic structure was obtained with relatively low cooling rate.

Economical aspect has been the foremost reason why ferromanganese powders have not become common practice in the PM industry. Cheap ferromanganese powders have long been attractive to the PM industry, however the cost associated with generating low dew point sintering atmosphere has prevented commercial use. For example, the attraction of cheaper ferromanganese powder relative to Ni powder is lost once dissociated ammonia atmosphere approaches dew point -55°C (30 ppm moisture). However there are technological reasons as well preventing use of fine ferromanganese powders. The dimensional and mechanical behaviour of sintered steels in which the Mn alloying elements are admixed is influenced greatly by agglomeration and segregation before the pressing process. This result in localised lower or higher alloying contents (chemical inhomogeneities). Agglomerated ferromanganese powder result in unacceptably large Mn-rich or pure Mn areas in the sintered steels as well as areas lean in Mn content. Finer powders are difficult to blend without agglomeration using conventional mixing technology. Powder mixes may segregate during handling causing compositional variations and hence dimensional variation between compacts. Agglomeration and segregation not only negates the benefits of improved distribution and higher mechanical properties attributed to fine powders, but also lead to failure. This segregation can be minimised using organic binder. Bonding of ferromanganese to Fe powder by resin should result in no perceivable difference in handling to the end user. The use of manganese and chromium for PM applications will be possible by binder-treated premix technology of a highly compressible pre-alloyed low alloy base material (Astaloy CrL, Astaloy CrM etc.).

The mechanical properties of investigated PM steels appear comparable to other studies [2, 9, 10, 13]. The strength results shoved strong dependence on the sintering atmosphere (H₂, N₂), especially for tempered steels. A comparison of the tensile strength, elongation and impact values found quite good agreement. The effect of using a higher sintering temperature than 1120°C on mechanical properties is evident from the presented results. The tensile and transverse rupture data shoved a measurable effect of the sintering temperature and tempering time. Increasing Cr content from 1.5% to 3% and/or tempering time offered improvement in properties under conditions employed. The application of semi-closed container offers a means to increase the mechanical properties of single compacted manganese steels to those typical of double pressed and sintered steels. Most significantly, the properties of the sinter-hardened manganese and manganese-chromium-molybdenum steels produced by single compaction exceeded those of the double pressed, double sintered and heat-treated commercial PM steels.

The work carried out has described the advantages of adding ferromanganese powder to Fe-Cr-Mo-C sintered powder compacts. We are interested in the N₂-sintering route to reduce H₂ levels in furnace gases to level less than that which is explosive in the air in the range 4-74.5%. It was therefore felt necessary to study the influence of type of sintering atmosphere on the utilisation of Mn and Cr additions to obtain better economical results and suitable safety precautions. The work was carried out using N₂/H₂ atmosphere with a dew point of below -60°C, so that it is not difficult to make a direct comparison with results obtained in industry, and with other published work, where different N₂/H₂ atmospheres had been used. Dew point refers to the dryness of a H₂ only atmosphere; if dilute (given water vapour content), the reducing potential is reduced, because the amount of H₂ is reduced. In flowing N₂ atmosphere, reduction of MnO oxides by solid carbon below 1425°C is impossible. Only control of the local microclimate in semi-closed container, i.e. CO/CO₂ ratio, ensures optimum conditions for thermocarbonic oxide reduction and efficient sintering [2]. Regarding microstructures of the investigated steels, N₂ with a dew point of -60°C proved as successful a furnace atmosphere as equally dry H₂. It is therefore concluded that, provided sintering of Fe-3%Mn-(Cr)-(Mo)-0.3%C steels is carried out in a semi-closed container (with availability of carbon and manganese therein, in our case within the green compact), furnace atmosphere of dry N₂ is as effective in preventing formation of deleterious oxide networks as of dry H_2 , or of H_2 - N_2 mixtures. Specimens sintered at 1250°C and possessed higher mechanical properties, irrespective of the H₂-N₂ ratio in the furnace atmosphere. For the investigated steels the



tensile and transverse rupture strength were approximately directly proportional to the H₂ content in the sintering atmosphere. Chromium enhances, however, as compared with previous results [4], the detrimental effects of N2 on strength of the PM Mn steels. Nitrogen in solid solution improves hardness and produces little effect upon elongation and impact toughness. The effect of N₂ on brittle fracture of these steels should be investigated further, especially in regard to the "clustering" N₂ atoms about substitutional alloy atoms Cr and Mn. Quantitatively correlating properties with microstructure is a problem that exists even in the case of relatively simple structure such as those consisting of a finely dispersed phase inside inhomogeneous matrix. In case of the structures discussed herein, the problem was considerably complicated in specimens cooled with cooling rate 65°Cmin⁻¹ because four constituents were present simultaneously: very fine pearlite (troostite), bainite, martensite and retained austenite. This is the reason why we restricted ourselves to some general remarks regarding a possible correlation between the cooling rates and the structure and mechanical properties of PM Fe-3%Mn-(Cr)-(Mo)-0.3%C steels. Many factors can be considered to explain the investigated steels strength: inherent strength of bainite, solid solution hardening of the ferrite, obstacles placed by the austenitic-martensitic island, presence within the structure of an appreciable percentage of martensite resulting from partial transformation of the stabilised austenite. However, the user is interested in the mechanical properties of bainitic structures, and it appears possible to relate the tensile strength, impact toughness and ductility to microscopic factors such as the bainitic grain size, and the size and distribution of carbides. In the various investigations conducted in connection with the morphology and mechanical properties of steels cooled at a cooling rate of 65°Cmin⁻¹, we observed numerous aspects of the so-called bainitic structures. In the investigated steels, a bainitic structure was obtained by the direct quenching of austenite. This structure exhibited not only a high tensile strength but also impact properties than approach those of tempered martensite. However, in the case of these self-hardening steels, it is practically impossible to obtain a bainite with a structure similar to that of tempered martensite by continuous cooling due to presence of acicular martensite. Self-hardening PM steels which produce the martensitic structure even if the cooling rate is quite low are susceptible to high residual stresses and cracking. With decreasing transformation temperature, there is a greater expansion during the bainitic transformation, and this leads to a higher level of internal stresses at the lower transformation temperatures. Bainitic structures require to be tempered at 200°C to achieve a combination of

optimum strength and ductility. With respect to the microstructures and mechanical properties of the investigated steels, we found that the investigated steels can be successfully sintering at 1250°C.

Acknowledgements

The financial support of the Ministry of Science and Higher Education under the contract no **N N507 477237 (AGH no 18.18.110.961)** is gratefully acknowledged. The results of this work were also presented during 2010 PM World Congress&Exhibition, Florence, Italy, 10-14.10.2010.

REFERENCES

- [1] S.C. Mitchell, A.S. Wronski, A. Cias, M. Stoytchev, Proc. PM²TEC'99, MPIF, Princeton, New Jersey 2, Part 7 P/M steels, 129 (1999).
- [2] A. Cias, Development and Properties of Fe-Mn-(Mo)-(Cr)-C Sintered Structural Steels (AGH-UST, Uczelniane Wydawnictwo Naukowo-Dydaktyczne, Kraków 2004).
- [3] M. Sulowski, A. Cias, Proc. PM 2004 World Congress & Exhibition, EPMA, Vienna, Austria 3, 93 (2004).
- [4] M. Youseffi, S.C. Mitchell, A.S. Wronski, A. Cias, Powder Metall. 43, 353 (2000).
- [5] M. Sulowski, A. Cias, M. Stoytchev, T. Andreev, Mater. Sci. Forum, ed. 2006, part 1, 534-536, 753 (2007).
- [6] A. Cias, S. C. Mitchell, Powder Metallurgy Progress 5, 82 (2005).
- [7] A. C i a s, Powder Metallurgy Progress **5**, 3, 147 (2005).
- [8] A. Cias, S.C. Mitchell, A. Watts, A.S. Wronski, Powder Metall. 42, 3, 227 (1999).
- [9] A. Cias, S.C. Mitchell, K. Pilch, H. Cias, M. Sulowski, A.S. Wronski, Powder Metall. 46, 2, 165 (2003).
- [10] M. Sulowski, The structure and mechanical properties of iron-manganese-carbon PM structural parts (Ph.D. Thesis, AGH-UST, Cracow, 2003, in Polish).
- [11] S.C. Mitchell, A. Cias, Powder Metallurgy Progress 4, 3, 132 (2004).
- [12] EC Directives 67/379/EEC and 67/548/EEC.
- [13] A. Ciaś, M. Sułowski, S. C. Mitchell, A. S. Wronski, Proc. PM2001 Powder Metallurgy Congress and Exhibitions, EPMA, Nice, France, 22-24.10.2001, v. 4, 246.
- [14] S. C. Mitchell, A. S. Wronski, A. Ciaś, Proc. XVIth Physical Metallurgy and Materials Science Conference, Gdansk–Jurata, Inzynieria Materiałowa 5 (124) Rok XXII, 633 (2001).