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CH. FIAŁ[*], E. DUDROVA[**], M. KABATOVA[**], M. KUPKOVA[**], M. SELECKA[**], M. SUŁOWSKI[*,♯], A. CIAŚ[*]

SINTERAUSTEMPERING OF TWO Mo-(Cu)-(Cr)-(Ni)-(Mn)-C STEELS IN A SEMI-CLOSED CONTAINER IN FLOWING NITROGEN

ZABIEG SINTERAUSTEMPERING DWÓCH STALI Mo-(Cu)-(Cr)-(Ni)-(Mn)-C SPIEKANYCH W PÓŁHERMETYCZNYM POJEMNIKU W ATMOSFERZE AZOTU

Three types of heat treatment, sinteraustempering in 500°C, 400°C and 350°C; sinterhardening and sintering with cooling at the rate 10K/min) as the final operation, on steels sintered semi-closed container were investigated. Results of mechanical properties, microstructure investigations and fracture and EDX analyses are reported. The study involved two PM steels: DH-1 (Fe-2%Cu-1.5%Mo-0.5%C) and 34HNM (Fe-0.2%Mo-0.8%Mn-1.5%Cr-1.5Ni-0.4%C). Prealloyed Höganäs DH (Direct Hardening) iron powder and graphite powder (grade C-UF) were used to produce DH-1 steel. Prealloyed Astaloy CrL iron powder, low carbon ferromanganese, elemental nickel and graphite grade C-UF powder were the starting powders of 34HNM steel. Pressing was in rigid dies at 660MPa according to PN-EN ISO 2740 standard. After compaction, green compacts were sintered in a specially designed semi-closed container at 1120°C for 60 minutes in a nitrogen atmosphere. The chemical composition of the sintering atmosphere was modified by adding ferromanganese and/or activator into the container.

All specimens were tested for tensile strength (UTS), elongation (A), yield offset strength ($R_{0,2}$), TRS, apparent surface and cross section hardness (HV 30). The best combination of strength and plasticity for both steels was achieved after sinteraustempering at 500°C. The results show that, using the specially designed semi-closed container, sinteraustempering in N_2 atmosphere offers the same or even better mechanical properties in comparison with sinteraustempering in vacuum. It means that sinteraustempering in N_2 atmosphere is a very interesting process in terms of cost in comparison with vacuum sinteraustempering.

Keywords: semi-closed container, sinteraustempering, sintering, nitrogen, microstructure, mechanical properties

W pracy przedstawiono wpływ trzech typów obróbki cieplnej (sinteraustempering w temperaturze 500°C, 400°C oraz 350°C, sinterhardening oraz chłodzenie po spiekaniu z prędkością 10K/min) zastosowanej dla stali wytworzonych techniką metalurgii proszków. Badania obejmowały dwie stale: DH-1 (Fe-2%Cu-1.5%Mo-0.5%C) oraz 34HNM (Fe-0.2%Mo-0.8%Mn-1.5% Cr-1.5Ni-0.4%C). Do produkcji pierwszej stali posłużył stopowy proszek żelaza Höganäs DH (Direct Hardening). W skład mieszanki drugiej stali weszły m.in. proszek żelazomanganu, stopowy proszek Astaloy CrL oraz elementarny proszek niklu. Do obu mieszanek proszku węgiel dodano w postaci proszku grafitu C-UF. Wypraski zostały przygotowane zgodnie z normą PN-EN ISO 2740, zostały one sprasowane pod ciśnieniem 660 MPa. Spiekanie (temp. 1120°C, t = 60min) oraz późniejsze operacje obróbki cieplnej odbywały się w laboratoryjnym piecu rurowym w pół-hermetycznym pojemniku z dodatkiem żelazomanganu w atmosferze azotu. Spieki poddano badaniom własności mechanicznych, badaniom mikrostruktury i faktograficznym oraz analizie EDX. W skład badań własności mechanicznych weszły: próba wytrzymałości na rozciąganie, próba odporności na trójpunktowe zginanie oraz badania twardości. Dodatkowo wyliczono wartości wydłużenia oraz umownej granicy plastyczności. Najlepszą kombinację własności wytrzymałościowych i plastycznych dla obu stali wykazano po obróbce sinteraustempering w temperaturze 500°C. Wyniki wskazują, że zastosowanie pół-hermetycznego pojemnika przy operacji sinteraustempering, z wykorzystaniem atmosfery N_2, pozwala na uzyskanie takich samych, bądź lepszych własności mechanicznych w porównaniu do operacji sinterhardening w próżni. Pozwala to na stwierdzenie, iż sinteraustempering w atmosferze azotu okazuje się być konkurencyjnym procesem w stosunku do procesu sinterhardening w piecu próżniowym.

1. Introduction

Currently, a considerable segment of the production of powder metallurgy products are sintered steel machine parts, manufactured on a mass scale. For the production of structural sintered steels, which are used mainly in the automotive industry and construction machinery, almost only link belt furnaces operating in a continuous manner are used today. Definitely more expensive and more costly in exploitation are furnaces equipped with a sophisticated accelerated cooling modules and they are used for sintering ending in sinterhardening [1]. In the sinterhardening technology, martensitic or

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[*] AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZ 30, 30-059 KRAKÓW, POLAND

[**] INSTITUTE OF MATERIALS RESEARCH SLOVAK ACADEMY OF SCIENCE, WATSONOVA 43, KOSICE, SLOVAKIA

[♯] Corresponding author: sulek@agh.edu.pl

martensitic+bainitic microstructure is obtained in the sintering furnaces, thus eliminating subsequent quenching and tempering heat treatments [2]. This process has several advantages, including reduction of the cost production and avoidance of contamination with oil quenching section. Sinterhardening can be performed in different ways, including the use of ovens equipped with an accelerated cooling zone [3]. For the performance of the sinterhardening operation of sintered steel, it is necessary to use steel powder with a higher than normal relative hardenability than the most commonly used steels produced by powder metallurgy technique [4].

The second direction, gaining recently some interest, and also an alternative way for the production of sintered products, is heat treatment called sinteraustempering. For sinteraustempering, the steel is cooled down rapidly from the sintering temperature to the bainitic region, then isothermally annealed to complete the bainitic transformation and subsequently cooled to room temperature. The resulting steel with a bainitic structure is less hard than steel hardened to martensite, but also more ductile than steel obtained by quenching to martensite and tempered to the same hardness. A disadvantage of this process is the relatively high temperature (~500°C) of annealing, encouraging oxidation. One of the solutions of this problem is to use a vacuum furnace [5]. However, due to the significant cost of this solution, a second, more affordable way, is the use of semi-closed container (Fig 1.) with a getter addition [6] and N_2 atmosphere, proposed by Ciaś [6 and 7] and Fiał et al [10].

Another method of heat treatment of PM steels, which allows a full transformation of the austenite into bainite, is austempering [8]. In work [9] the authors proposed a bainitic quenching of Fe-1.5Cr-0.2Mo-0.6C PM steel in molten salts or in fluidized bed as the operation after sintering. It is one interesting method, nevertheless environmental and handling problems should be considered.

The medium to high alloy steels, which contain elements with a high affinity for oxygen, e.g. Cr, Mn, and Si, are, in general, difficult to sinter. The possibilities of using semi-closed containers for conventional sintering in flowing gases (nitrogen, nitrogen-hydrogen, even air) have been recently investigated by Cias [6, 7]. The author [7] developed the use of a semi-closed containers to sinter in nitrogen Cr and Mo containing steels. DH-1 and 34HNM steels have molybdenum in their composition – maybe this is the solution to the problem of its high affinity for oxygen.

In this paper the results of investigations of two PM steels containing molybdenum and chromium, sintered in semi-closed container in pure nitrogen atmosphere using sinterhardening and sinteraustempering are described.

2. Experimental procedures

The aim of this study was to investigate the effect of different types of post-sintering heat treatment on the mechanical properties and structure of sintered steel. Compositions of the tested steels are given in Table 1.

To produce DH-1 PM steel, pre-alloyed iron powder Distaloy DH (Direct Hardening) containing Fe-2% Cu-1.5%Mo was used. This powder – by its composition – is characterized by high hardenability. In the preparation of 34HNM steel, chromium and molybdenum were introduced in the form of alloy Astaloy CrL, low carbon ferromanganese (Fe-77% Mn-1.3% C) and elemental nickel powders were added. For both steels, carbon was introduced into the mixtures in the form of Höganäs graphite powder grade C-UF.

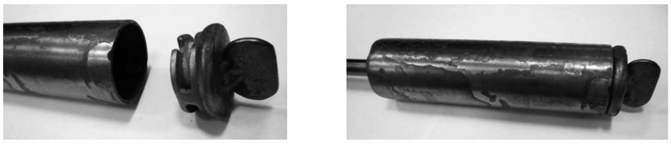
TABLE 1

Chemical composition of tested steels (mass %)

Mixture	Fe	C	Cu	Mo	Cr	Ni	Mn
DH-1	96	0.5	2.0	1.5	-	-	-
34 HNM	95.6	0.4	-	0.2	1.5	1.5	0.8

The mixing was performed in a Turbula mixer for 60 minutes. During mixing no lubricant was used. The powders were single-action compacted into ISO 2740 dog-bone tensile test bars in a steel die at 660 MPa.

Sintering was carried out in a laboratory horizontal tube furnace at 1120°C for 60 minutes with the flowing nitrogen being dry (10 ppm moisture) in semi-closed container (Fig. 1) (containing also lumps of ferromanganese), employing convective (65°C/min) cooling. Then the compacts were subjected to various variants of heat treatment after sintering process, in batches of up to 5 pieces. The conditions of heat treatment after sintering and the designation are presented in Table 2.



a) With open seal b) Closed with samples, ready for sintering

Fig. 1. A semi-closed container, designed by A. Ciaś

After sintering and heat treatment physical and mechanical properties of sintered steels were determined. Also microstructure investigations were carried out. Fracture and EDX analyses of sintered steel were performed in collaboration with the Institute of Materials Research, Kosice.

TABLE 2

The description of the post-sintering heat treatment conditions

Steel	Heat treatment type	Time	Temperature	Designation
DH-1	Isothermal annealing	60 minutes	500°C	SAT 500
			400°C	SAT 400
			350°C	SAT 350
	Sintering + tempering		200°C	S+H
	Cooling rate [10K/min]	-	-	S+C
34HNM	Isothermal annealing	60 minutes	500°C	SAT 500
			400°C	SAT 400
			350°C	SAT 350
	Sintering + tempering		200°C	S+H
	Cooling rate [10K/min]	-	-	S+C

3. Results

The study included two steels with different chemical compositions, subjected to three different cycles of thermal sintering operation. Density of compacts and sintered samples were determined using the geometric method. Density measurements, d_0 and d_1, are shown in Table 3.

TABLE 3

Green and as-heat treated densities of steels – mean values and standard deviations

Steel	Processing variant	Green density d_0, g/cm^3	As –heat treated density d_1, g/cm^3
DH-1	SAT 500	6.69±0.04	6.65±0.07
	SAT 400	6.66±0.08	6.64±0.07
	SAT 350	6.69±0.11	6.63±0.10
	S+H	6.68±0.06	6.67±0.06
	S+C	6.76±0.02	6.73±0.02
34HNM	SAT 500	6.78±0.01	6.73±0.02
	SAT 400	6.74±0.01	6.69±0.01
	SAT 350	6.76±0.01	6.72±0.04
	S+H	6.72±0.02	6.71±0.04
	S+C	6.65±0.05	6.62±0.05

The data presented in Table 3 shows that d_1 is lower than d_0 by about 0,5% for both DH-1 and 34HNM steels. The reason of decrease in the densities can be the changes in the material during sintering – the reduction of the oxides. The samples were mechanically tested on a MTS tensile-testing apparatus at a rate of 1 mm/min and in three-point bending on a ZD-10 tester using a jig with a span of 28.5 mm, at a crosshead speed of 2 mm/min. The yield strength refers to 0.2% offset. Hardness (HV30) was measured on Innovatest Nexus Series. The results of mechanical testing are shown in Tables 4 and 5.

Analyzing the results of investigations, presented in Table 4 and 5, it can be seen that the highest values of UTS of DH-1 and 34HNM steels are obtained after sinteraustempering 500°C. In addition, in the case of variant SAT 500 in DH-1 steel, the smallest value of standard deviation, 67 MPa, was observed. It is worth to note that for 34HNM steel tensile strength (UTS) reached 753 MPa and was nearly 80 MPa higher than the UTS value for that steel after sinterhardening. In the case of 34 HNM steel, the differences of UTS values between other variants were much smaller. Both tested steels were subjected to sinteraustempering heat treatment at 500°C, characterized by the highest value of elongation at break – DH-1 steel – 0,7% and 34HNM steel – more than 1%. Data presented in Tables 4 and 5 show that the results of a strength tests strongly depend on the post-sintering heat treatment. For both tested steels, the highest value of TRS was observed after the SAT variants, except for the DH-1 and 34 HNM steels annealed at 400°C and 500°C, respectively. The hardness test results were different on the surface and at the cross section of the tested samples. For DH-1 steel, the hardness on the surface, in the case of each variant of heat treatment, is greater than the cross-sectional hardness. Quite an inverse relationship was observed when hardness of 34HNM steel was measured. To examine microstructures by light microscopy, a Leica DM4000M and Leica DM LM instruments were employed. Metallographic investigations were carried out on 3% Nital etched samples. The characteristic microstructures of SAT 500 variant for both steels are shown in Figs. 2-3.

TABLE 4

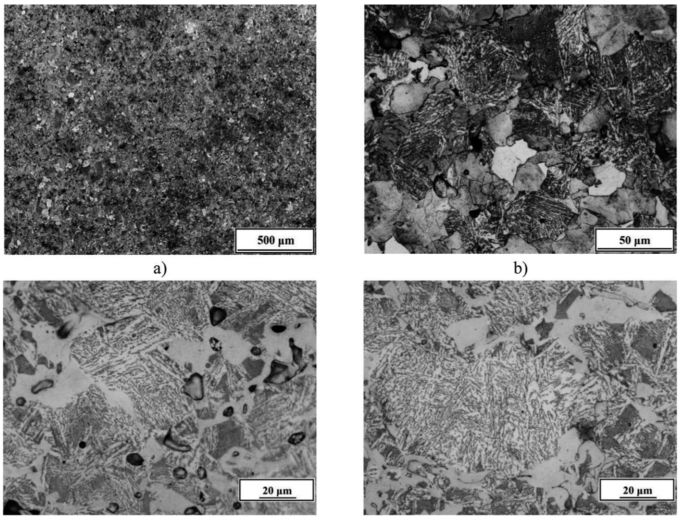
Mechanical properties of DH-1 sintered steel

Processing Variant	Yield Strength, MPa	A, %	UTS, MPa	TRS, MPa	HV30 (apparent)	HV30 (cross section)
SAT 500	413±50	0.7±0.1	514±68	1548±173	207±14	195±7
SAT 400	389±61	0.5±0.2	483±84	1571±70	180±16	171±8
SAT 350	355±55	0.5±0.2	446±125	1360±193	178±13	167±27
S+H	353±86	0.5±0.2	439±77	1460±101	175±23	166±25
S+C	387±55	0.6±0.2	489±76	1474±137	180±28	188±11

TABLE 5

Mechanical properties of 34 HNM sintered steel

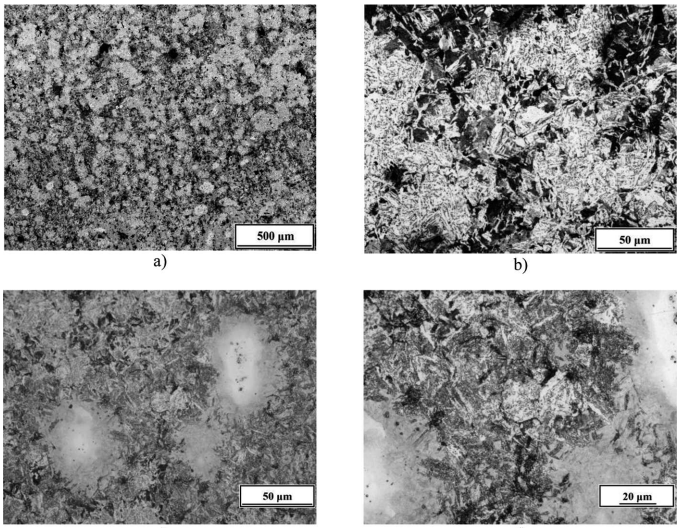
Processing Variant	Yield strength, MPa	A, %	UTS, MPa	TRS, MPa	HV30 (apparent)	HV30 (cross section)
SAT 500	409±21	1.1±0.2	753±67	1414±194	244±28	272±16
SAT 400	436±22	0.9±0.2	668±60	1301±274	213±36	270±18
SAT 350	403±31	0.8±0.3	636±104	1292±204	216±20	252±16
S+H	432±38	0.8±02	674±92	1347±139	223±30	266±14
S+C	393±27	0.8±0.2	604±49	1361±188	218±25	290±16



a) b) c) d)

Fig. 2. The characteristic microstructures of DH-1 PM steel after SAT 500 variant (a, b – Leica DM4000M; c), d) – Leica DM LM

The microstructures shown in Figure 2 consists of upper bainite (90-84 at.%Fe, C), areas of very fine bainite (EDX: 1-1.7at.%Mo, 78-92 at.% Fe, C) and relatively large Cu-rich areas with rich precipitated epsilon phase (EDX: 0.8 at.%Mo, 10 at.%Cu, 77 at.%Fe, C), mostly surrounded by very fine bainite (Fig 2c and 2d).

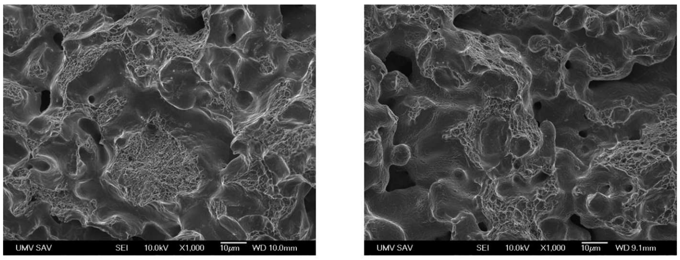


a) b) c) d)

Fig. 3. The characteristic microstructures of 34 HNM PM steel after SAT 500 variant (a, b – Leica DM400M; c, d – Leica DM LM)

In the case of 34HNM steel after sinteraustempering at 500°C, the microstructure is heterogeneous, consisting of a bainitic matrix, areas alloyed with nickel (Ni-austenite, Ni martensite), areas alloyed with Mn (FeMnC) and remnants of ferromanganese particles. Because Ni was added as a carbonyl powder, it became agglomerated and so austenite/martensite areas are relatively large (Fig. 3c). In the unetched microstructure, fine and coarser oxide particles are visible. It seems that the boundaries of original austenite grains are “marked” with carbides.

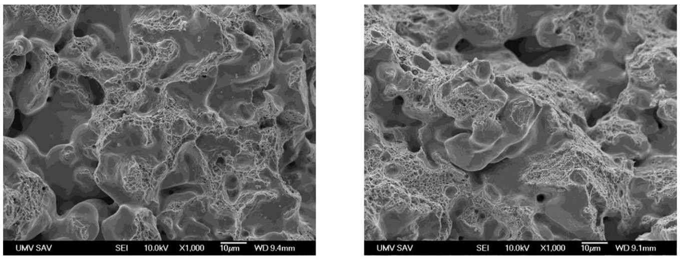
To examine fractures of investigated steels, a JEOL JSM 7000 F scanning electron microscopy, equipped with EDX, was used. The fracture surfaces of the differently processed steels are shown in Figs. 4 and 5.



a) After tensile test b) After bend test

Fig. 4. Characteristic fractographs of DH-1 PM steel after SAT 500 variant

Fractography of SAT 500 (Fig. 4) variant revealed interparticle ductile fracture with fine shallow dimples. Failure took place along surfaces of bainite packets when fine shallow dimples were initiated by fine carbides. Cu-rich areas with epsilon phase failed in a ductile mode with fine dimples and with local plastic flow. Coarse shallow dimples were initiated by spherical MnS inclusions (EDX: 41 at.%S and 42 at.%Mn, rest Fe). Rare transgranular cleavage facets were very small, up to 5 microns in size. Pores and fine particulates, e.g. FeMoC carbides, were detected. After TRS testing, very similar fracture behaviour was observed.



a) After tensile test b) After bend test

Fig. 5. Characteristic fractographs of 34 HNM PM steels after SAT 500 variant

In all three sinteraustempered variants (SAT 500, SAT 400, SAT 350), predominant was the interparticle ductile failure with fine and coarse shallow dimples, failure along prior particle surfaces initiated by oxide particles (complex Cr, Mn,[Si] oxides) and areas with fine shallow dimples, when the failure along bainite packets is initiated by carbides. In the vicinities of the remnants of original FeMnC particles, intergranular fracture facets were detected, typical feature of alloying through FeMnC particles. Development of local plastic flow was observed. In Figs. 6 and 7 the EDX analysis of investigated steels was presented.

Example areas of DH-1 steel, shown in Figure 6, were tested for the elemental content. It can be shown that the distribution of elements in these areas is uneven (2,68%C, 1,16%Cu, 2,63%Mo, 93,53%Fe for spectrum 3 and 4,09%C, 5,23%Cu, 2,43%Mo, 88,25%Fe for spectrum 5). There is a high carbon content, the copper content is not uniform and the amount of molybdenum and iron is variable.

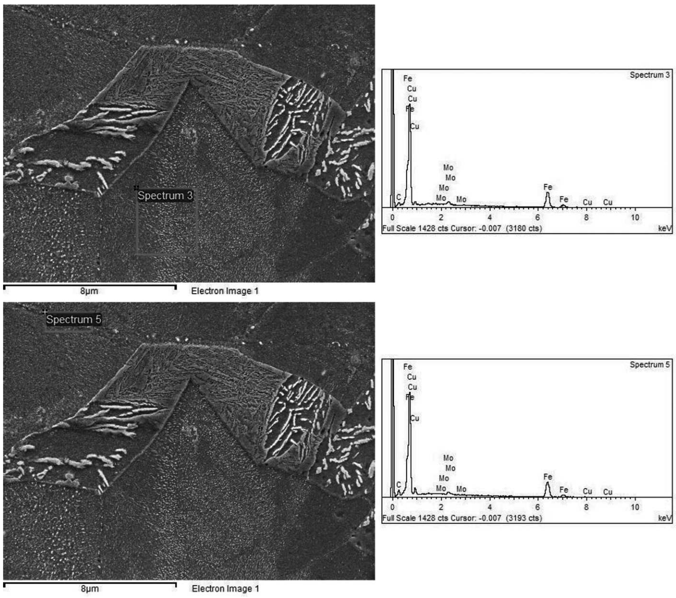


Fig. 6. Results of EDX analysis for DH-1 steel after SAT 500 variant

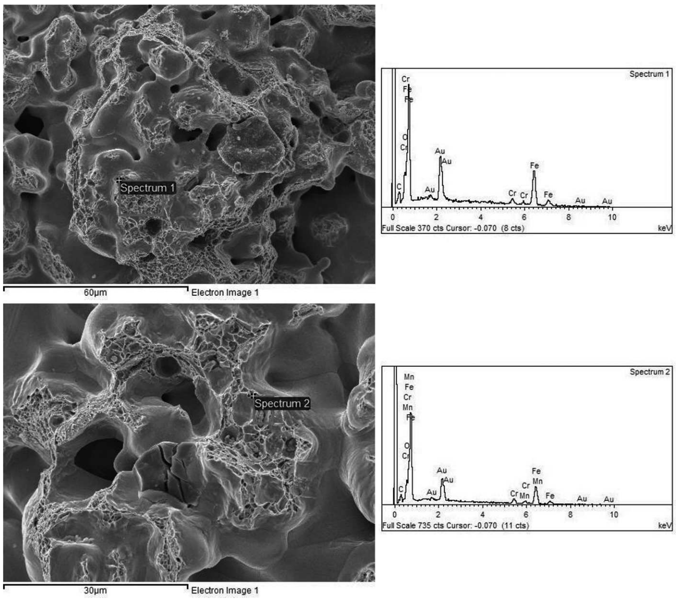


Fig. 7. Results of EDX analysis for 34HNM steel after SAT 500 variant

For EDX analysis of 34HNM steel, a lower carbon content in the examined areas was observed, however, oxygen has appeared. Distribution of other elements in the steel is also non-uniform and even some elements were not detected during the analysis – Mn in the range of spectrum 1, and nickel in both spectra.

4. Discussion

Among the metallurgical features of DH-1 and 34HNM steels, probably the most important are high bainitic hardenability and possibility to formation of stable and competing alloy carbides. The ability to high bainitic transformation means that steel transforms to a fully bainitic microstructure over a wide range of cooling rates. This feature makes the steel suitable for sinteraustempering.

Mechanical properties after sinteraustempering in 500°C for both steels are higher than those attainable with sinterhardening, additionally steel samples after sinteraustempering do not require any tempering – which causes cost saving. It should be noted that sinteraustempering at 500°C also gave marginally the best combination of strength and plasticity for DH-1 and 34HNM steels.

It is reassuring that all the specimens, for both steels, regardless of heat treatment variations, exhibited ductility. This demonstrates that use of proposed semi-closed containers and pure nitrogen atmosphere can be extended from conventional sintering technology to sinterhardening and sinteraustempering.

The results obtained can be compared with the results presented by Girardini et al. [5], who investigated Fe-3% Cr-0.5 Mo -0.35/0.5 C system, but by vacuum processing. They reported that, once the cooling strategy has been set up, austempering was combined to sintering in a single sinteraustempering process aimed at obtaining a fully lower bainitic microstructure.

The mechanical properties of sinteraustempered steel investigated in [5] were slightly lower than those attainable with sinterhardening. The results of mechanical properties of DH-1 and 34HNM steels, obtained during this investigation are very promising. What is more, they are a slightly higher than those recorded for steel sinteraustempered in vacuum [5].

The further work is needed to optimise the sinteraustempering process of DH-1 and 34HNM steels – time and annealing temperature – to get even better properties than presented in this paper.

The above results showed the possibility to combine high temperature sintering with a controlled cooling in a semi-closed container in pure nitrogen atmosphere, may be exploited to carry out sinterhardening with optimum cooling rate and sinteraustempering with optimum temperature for a specific PM steel.

5. Conclusions

On the basis on the results presented, the following conclusions can be drawn:

1. The most important result of these studies is that the semi-closed container processing is a satisfactory technique, on a laboratory scale, for sinterhardening and/or sinteraustempering.
2. Reviewing above results of DH-1 steel (Fe-2Cu-1.5Mo-0.5C) and 34HNM steel (Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn -0.4C), it can be mentioned that both steels have been processed successfully, all specimens exhibiting ductility, using conventional PM, sinterhardening and/or sinteraustempering experimental procedures.
3. The preliminary results did not detect marked differences between various heat treatments, but show, for both steels, that sinteraustempering is the optimum (so far explored) processing procedure.
4. The best combination of strength and ductility was recorded for sinteraustempering at 500°C for both steels - Fe-2Cu-1.5Mo-0.5C (DH-1) and Fe-0.2Mo-1.5Cr-1.5Ni-0.8Mn -0.4C (34HNM): UTS –

514 and 753 MPa, TRS – 1548 and 1414 MPa, yield 0,2% offset – 413 and 409 MPa, elongation A – 0,7 and 1,1% respectively.

5. The further investigation of sinteraustempering of 34HNM steel is needed to show that combination of sintering in a semi-closed container plus sinteraustempering process in N_2 atmosphere results in the same or better properties of steel than those after processing in vacuum.

Acknowledgements

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