

OPTIMISED PROPERTIES OF MOLYBDENUM PM STEELS BY ADVANCED CASE HARDENING PROCESS

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Abstract

Powder metallurgy is one of the industrial manufacturing techniques growing in importance world-wide. Applications in heavy-duty components like gears, pistons and connecting rods that are exposed to high cycle dynamic loads can be realised with new developed materials and processes. A pre-alloyed molybdenum steel powder has been developed that can be used to manufacture high density P/M parts. The MSP 3.5 Mo is characterised by its very high density of 7.50 g/cm^3 as a result of α -phase sintering. The MSP 3.5 Mo was improved with regard to its strength and toughness properties by optimising the alloying system and the case hardening process. The strength behaviour of the material was initially examined in extensive material science test programmes. The detailed characterisation of this material, which is presented in this paper, confirmed that the MSP 3.5 Mo casehardened by using plasma technology comes very close to meeting the stringent requirements of highly-loaded P/M parts, such as gears.

1. Introduction

Compared to machining, powder metallurgy constitutes an extremely economical method of gear component manufacture. The economical and environmentally compatible PM process is a near-net-shape forming method and can open new and innovative application potentials for powder metallurgy in the transportation and automotive field. The implementation of PM components in automotive applications increases continuously, in particular for higher loaded gear components like synchromesh mechanism. The because of the porosity frequently inadequate material and component properties of the PM materials currently prevent the application e.g. at automobile gears that are subject to high loads. By increasing the density of sintered components the mechanical properties are improved. In order to increase the density a number of different methods have been developed or are still in developing like partial densification or warm compaction. A conventional method of attaining high component density is shrinkage during sintering. The most effective way of increasing shrinkage with sintered steels is to execute sintering in the ferritic phase (α -phase). In the ferritic phase, the diffusion coefficient of Fe is approximately 100 times higher than in the austenitic phase (γ -phase). The self-diffusion of iron in iron can be calculated as follows [1]:

$$D = D_0 \exp\left(\frac{-H_D}{kT}\right)$$

- D = diffusion constant in cm^2/s
 D_0 = material-dependent diffusion constant in cm^2/s
 H_D = activation energy in eV
 k = Boltzmann constant = $1.38062 \cdot 10^{-23} \text{ J/K}$
 T = temperature in K

This finding inspired the development of the QMP MSP 3.5 Mo water atomised, pre-alloyed steel powder with a molybdenum content of 4.0 wt-%. Because of this molybdenum content the sintering behaviour of the material is constant during the high temperature sintering process. The outstanding property of this material is the component density of 7.5 to 7.6 g/cm^3 (approx. 95% of the theoretical density) that can be achieved by single sintering without a liquid phase.

2. Establishing suitable alloy systems

The fact that molybdenum extends the ferritic zone of iron is known in literature. Therefore the Fe-Mo system seems promising for P/M materials sintering exclusively in the α -phase. The Fe-Mo phase diagram was established on the basis of dilatometric tests and thermodynamic calculations. As the material MSP 3.5 Mo is to sinter fully in the α -phase, knowledge of the exact boundaries of the different phases is indispensable. A phase diagram can be designed by means of dilatometric curves, see figure 1.

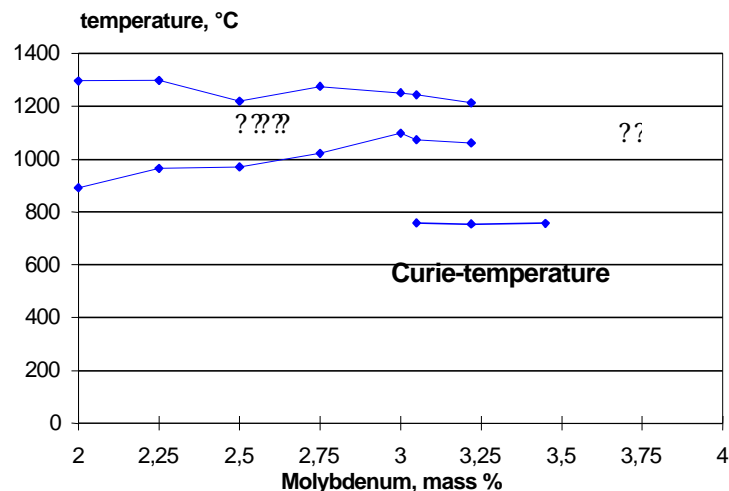


Fig. 1. Fe-Mo phase diagram established on the basis of dilatometric curves

With rising molybdenum content, the phase region $\alpha + \delta$ is increasingly restricted. Up to a molybdenum content of 3.5 mass-%, a phase transformation $\alpha + \delta$ takes place while the material is heating up. With a molybdenum content of 4.0%, the dilatometer printouts did not show any transformation. With this Mo-content, the material is purely ferritic over the entire temperature range. The programs Chemsage and Thermocalc of the Institute of Ferrous Metallurgy (RWTH Aachen/Germany) [2] were used to calculate the ternary phase diagram Fe-Mo-C. On the one hand,

the diagram is intended to provide information on the stability of the γ -phase during carbon-free processing. On the other hand, the purpose of the calculation was to clarify how much of the alloying element carbon may be added at the very most to achieve nothing but the ferritic phase during the sintering process. In addition, the various phases undergone by the material in the course of case hardening, as a function of the austenitising temperature, were to be demonstrated.

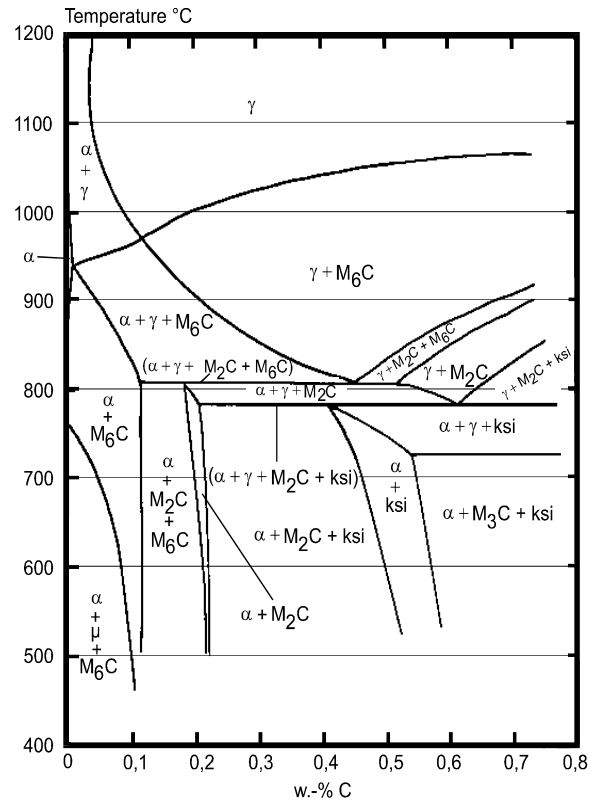


Fig. 2. Quasi-binary section through the Fe-Mo-C phase diagram at a molybdenum content of 3.5 mass-%

The effect of carbon on the Fe-Mo system is extremely complex. For the Fe-Mo-C phase diagram, quasi-binary sections at 3.5 mass-% were calculated (figure 2). The molybdenum content was kept constant in each case to avoid complicating the diagrams unnecessarily. On the one hand, the γ -zone is extremely restricted by carbon, with a maximum possible extension of the γ -phase up to around 940°C and approximately 0.01% carbon. Sintering must therefore be practically carbon-free in order to take advantage of effect of the high self-diffusion coefficient of iron in the γ -phase. Carbon should therefore be introduced into the material after sintering, for example by case hardening. On the other hand, the phase diagram shows that the usual austenitising temperatures of 850 – 950°C are not sufficient to decompose the M_6C carbides and to austenitise the material completely. Case hardening must be done at temperatures above 1050°C in order to avoid carbide precipitation.

The strength of MSP 3.5 Mo at about 350 MPa is still low. Therefore niobium and phosphorus were added to the basic powder to increase its strength. These elements do not constrict the ferritic phase. It was found out that merely partial alloying with phosphorus improves strength with elongation after fracture it's remaining the same. Niobium also seems promising although its strength-increasing effect only shows after carbon is added by a thermochemical treatment (case hardening), but not in the as-sintered condition.

3. Optimisation of case hardening

Various variants of the material MSP 3.5 Mo were case hardened to increase its strength additionally. When the samples were conventionally case hardened, first of all we had to deal with problems with carbide formations at the grain boundaries because of the high molybdenum content of the matrix. The solution temperature of the carbides is essential for case hardening since carbides at the grain boundaries substantially reduce strength and toughness properties. If low austenitising temperatures are selected for case hardening, Figure 2 shows that special carbides of the M_6C type appear at the grain boundaries, as demonstrated by EDX examinations. Solution annealing tests in the quenching furnace were run with three different case hardened material variants (Fe-3.5Mo, Fe-4.0Mo, Fe-4.0Mo0.1Nb) in order to verify the calculated Fe-Mo-C phase diagram. In the quenching furnace used, the sample temperature can be defined and set via a PC control system. After the annealing treatment, the samples can be quenched very quickly in a water bath. To achieve a carbide-containing initial condition, the austenitising temperature selected for case hardening was so low that carbides were produced, see Figure 3. The decomposition of the carbides can be subdivided into different stages. At an annealing temperature of 900°C , the carbide network still exists, but the carbides already start to coalesce as round structures (1st stage). The 2nd stage emerges after an annealing treatment at 1000°C . Now nothing but round, coalesced and coagulated carbides are visible. In the 3rd stage, individual carbides start to disintegrate, and from a temperature of 1050°C the percentage of carbides decreases noticeably. If an annealing temperature above 1100°C is selected, all carbides will disintegrate, see Figure 4. Therefore an austenitising temperature of more than 1050°C must be chosen for case hardening to prevent the formation of special carbides at the grain boundaries.

Subsequently, case hardening treatments including plasma carburisations were carried out at IPSEN International GmbH. The microstructure was examined by light-optical and scanning electron microscope, and the effective case depth over the sample width measured to DIN 30 911.

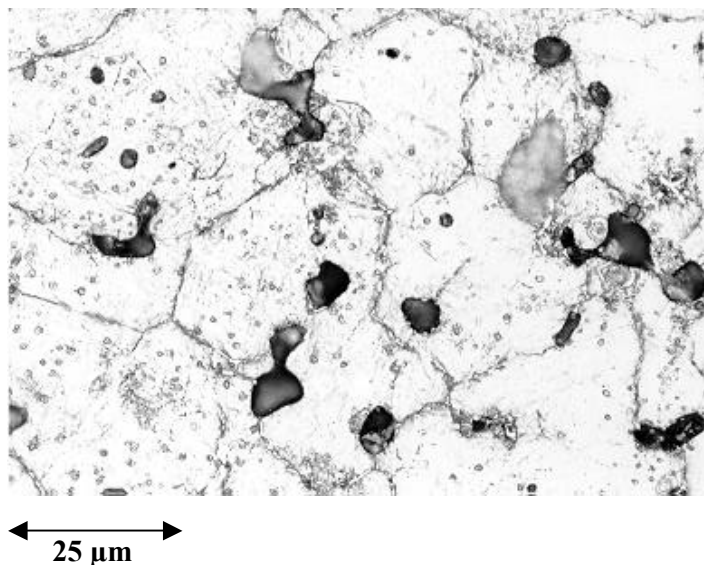


Fig. 3. Annealing temperature of 900°C : Carbide network at the grain boundaries, X = 1000

By case hardening, the hardness of the case can be increased significantly, since as a result of the introduction of carbon and the subsequent quenching the microstructure is transformed from ferrite into martensite. At first it has been investigated whether a single hardening treatment or direct hardening is preferable. In the event of direct hardening, the material is quenched right after coming out of the austenitising heat, whereas with single hardening, it is first cooled down to room temperature after carburisation, i.e. no hardening occurs. In this condition, the workpiece is easier to

submit to intermediate treatment or to straighten. Then hardening is performed. The results show that the performance of a direct hardening treatment is clearly better than that of a single hardening treatment. First, during the single hardening treatment carbides precipitate at the grain boundaries, see Figure 5. The SEM reproduction shows a triple point made up of three converging grain boundaries in the ferritic microstructure. Second, the single hardening treatment does not achieve a sufficient case hardness, as demonstrated in Figure 6.

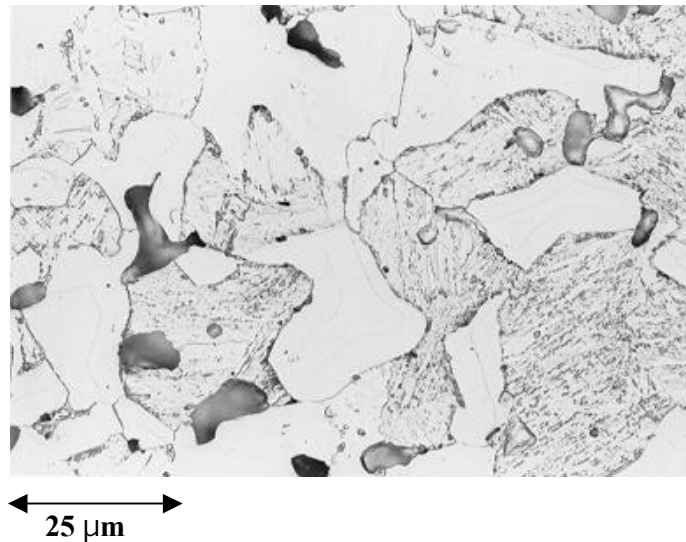


Fig. 4. Annealing temperature of 1100°C: Carbides have disintegrated; X = 1000

With the samples that were directly hardened at an austenitising temperature of 1080°C or above, hardly any carbides were formed at the grain boundaries, as shown in Figure 8. Even in 5000-fold magnification by the SEM, no carbides are visible at the grain boundaries. Then the influence of the temperatures of the direct hardening treatments on carbide formation and variations in hardness was compared. One part of the samples was directly hardened at 1080°C, the other part at 900°C. A significant amount of carbides occurred in neither of the variants. A high case hardness of more than 900 HV0.1 was determined, with even variations in hardness, as represented in Figure 7. Therefore the samples were case hardened at an austenitising temperature of 1080°C, followed by direct hardening at 900°C.

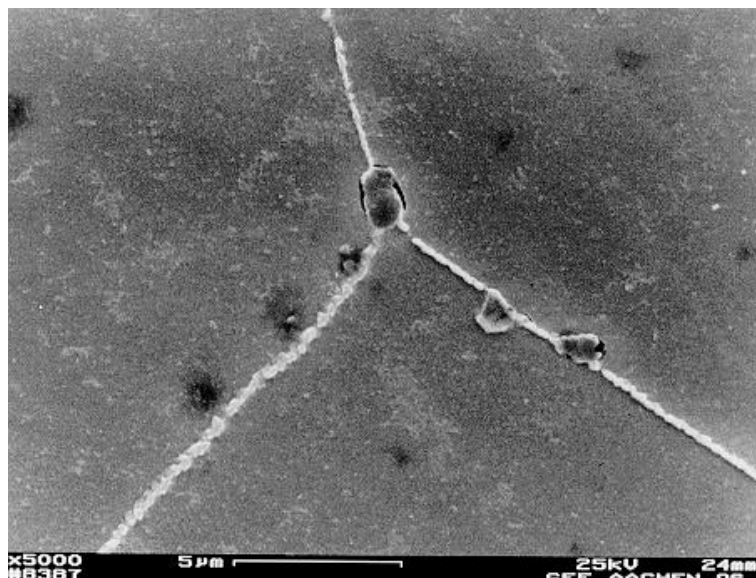


Fig. 5. MSP 3.5 Mo after single hardening: Carbides at the grain boundaries

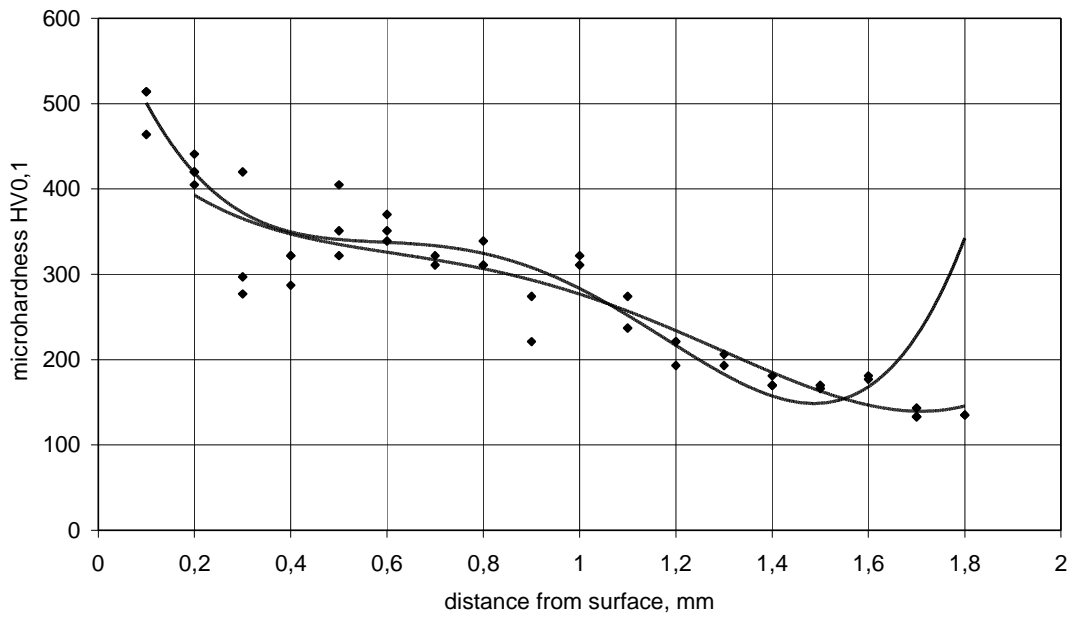


Fig. 6. Variations in hardness through the case hardened layer, MSP 3.5 Mo ($T_{\text{aust}} = 1100^{\circ}\text{C}$, single hardening treatment: 850°C)

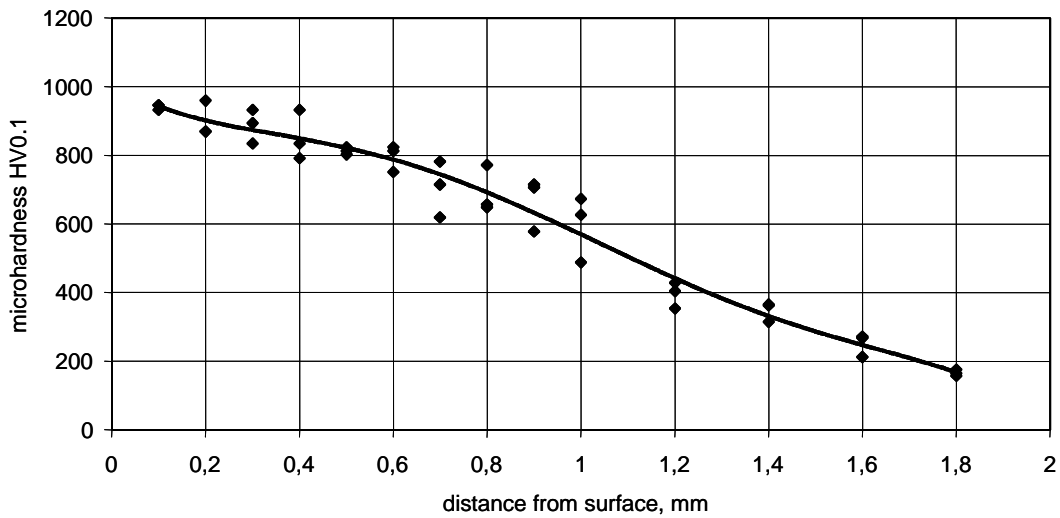


Fig. 7. Variation in hardness through the case hardened layer, MSP 3.5 Mo ($T_{\text{aust}} = 1080^{\circ}\text{C}$, direct hardening treatment: 900°C)

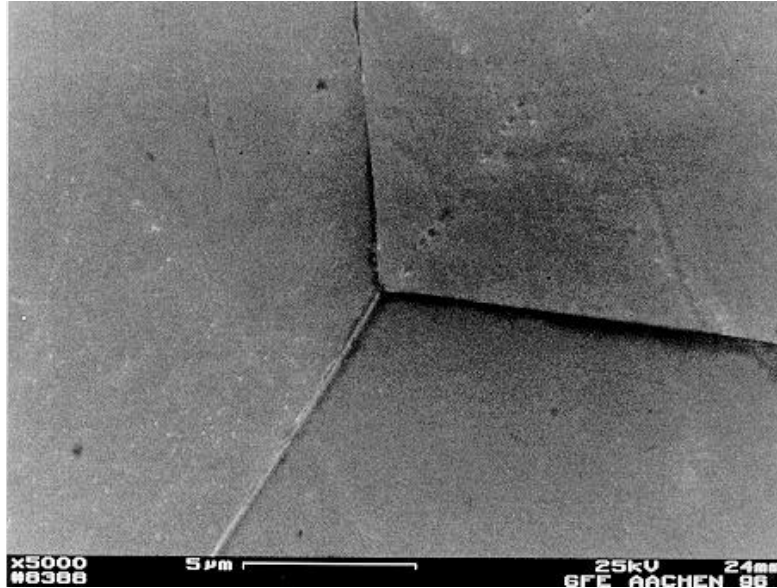


Fig. 8. Ferritic microstructure free from carbides

4. Heat treatment by using plasma-carburising furnace

As mentioned before, austenitising temperatures over 1050°C must be chosen for the case hardening process of sintered parts made from MSP 3.5 Mo. Figure 9 shows a single-chamber plasma-carburising furnace with high-pressure gas quenching which has been used for the above mentioned case hardening treatments. Such a single-chamber plasma-carburiser is being operated at IPSEN International GmbH in Kleve, Germany.

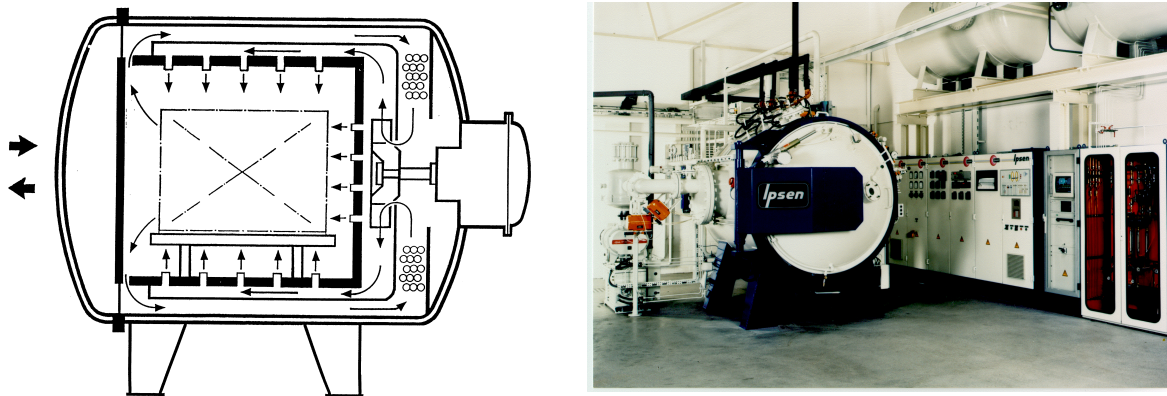
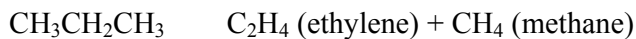
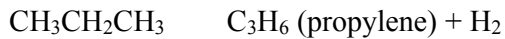


Fig. 9. Single-chamber plasma-carburising furnace VPHCN 36 x 36 (IPSEN International GmbH)

After evacuating the heating chamber to 10^{-2} mbar, the parts are heated-up in several steps up to the carburising temperature of 1080°C. The heating-up in several steps is necessary to avoid a distortion of the parts. The sputter-plasma (pure hydrogen), which is used for the cleaning and the activation of the surface of the parts, will be ignited during the heating-up process. The carburising occurs in several carburising and diffusion steps after a temperature compensation at carburising temperature. The pressure in the heating chamber is reduced to 2 mbar during the diffusion phase. Following the carburising and diffusion steps, and cooling to hardening temperature, the quench gas flows into the furnace chamber from all sides, being recirculated into chamber via a heat exchanger

and fan. The gas supply for the furnace comes from two buffer tanks, one filled with nitrogen (16 bar) and the other filled with helium (40 bar). Thus, gas pressures of up to 10 bar with nitrogen and up to 20 bar with helium or nitrogen/helium mixtures can be established in the furnace during quenching.

For the carburising process methane gas (CH₄) has been chosen. Methane has in comparison to propane the advantage, that the transfer of carbon occurs exclusively via the glow discharge or via moleculars which arise during the glow discharge. If propane is used, the heat treatment at temperatures over 600°C consists of a low pressure and plasma carburising. The thermal decay reaction for propane is [3]:



The boundaries between the carburised and non carburised areas will be not so exactly kept by using propane instead of methane due to the low pressure carburising component.

5. Gear tests

Gear tests ($m_n = 3.5 \text{ mm}$; $b = 20 \text{ mm}$; $\beta = 0^\circ$) for were performed using the molybdenum-containing materials listed in figure 10. For reasons of time and cost, circular blanks of the sintered materials were pressed in a simple die, the gear teeth were machined and the parts were heat-treated and ground. The circular blanks were manufactured at a pressure of $P_1 = 750 \text{ MPa}$. Sintering was carried out for $t_s = 30 \text{ min}$ at $1290 \text{ }^\circ\text{C}$ in an H_2/N_2 atmosphere. The density of the sintered rollers was $\rho_1 = 7.72 \text{ g/cm}^3$ for Variant 1 and $\rho_2 = 7.76 \text{ g/cm}^3$ for Variant 2. S/N-curves for the 20MnCr5 reference variant and the two sintered material variants (V1 and V2) were determined in pulsator tests. Some of the sintered gears were additionally shot-peened using compressed air in order to enhance the load carrying capacity of the tooth root and likewise tested in the pulsator. To save time and cost, the load-carrying capacity of the 20MnCr5 reference variant tooth root was not tested in the shot-peened state.

Figure 11 shows the S/N-curves for the conventional 20MnCr5 case-hardening steel reference variant and the V1 and V2 PM variants. The tooth root stress continuously withstood by the 20MnCr5 reference variant is approximately $F_0 = 900 \text{ N/mm}^2$. The equivalent value for the Variant 1 sintered gears is roughly 25 % below this figure, at $F_0 = 685 \text{ N/mm}^2$. The value for Variant 2 is $F_0 = 745 \text{ N/mm}^2$, or about 18 % below the reference variant. Shot peening increases the tooth root load-carrying capacity of the PM gears. Both PM variants achieve a continuously withstandable tooth root stress of $F_0 = 1000 \text{ N/mm}^2$ approx., which is 9 % above the tooth root load-carrying capacity of the unpeened reference variant.

Figure 12 contains the test points covered for Variant 2, indicating the hertzian pressure H_0 and the torque M_1 applied to the pinion. The varying moduli of elasticity for the pinion ($z_1 = 25$) and the gear ($z_2 = 26$) were taken into account in calculating the hertzian pressure.

In the case of the sintered material, the modulus of elasticity determined ultrasonically on the sintered rollers ($\rho = 7.63 \text{ g/cm}^3$) was employed. An S/N-curve for 16MnCr5 compact steel determined in earlier tests is also shown to indicate the comparative load-carrying capacities of sintered gears and 16MnCr5 compact gears. Results of the running tests show that the transition zone from fatigue strength to creep strength is comparable with that for steel. The continuously withstandable hertzian pressure for Variant 2 is roughly 97 % of that for the steel material (50 % probability of failure).

		V 1	V 2	Reference
alloy system		MSP3.5Mo	MSP3.5Mo -0,1%Nb	20MnCr5
compacting		P ₁ = 750 MPa t _s = 30 min		
sintering (mixed gas H₂/N₂)		S ₁ = 1290 °C		
density (g/cm³)		7,72	7,76	7,86
Young's modulus E (N/mm²)		185.000	186.000	210.000
\bar{E} (N/mm²)	$\bar{E} = \frac{2E_1E_2}{E_1+E_2}$	196.700	197.200	210.000

combination of gears:
test gear - counter gear

V1 - Reference
V2 - Reference
Reference - Reference

Reference: 20MnCr5

Fig. 10. Work material variants and production parameters

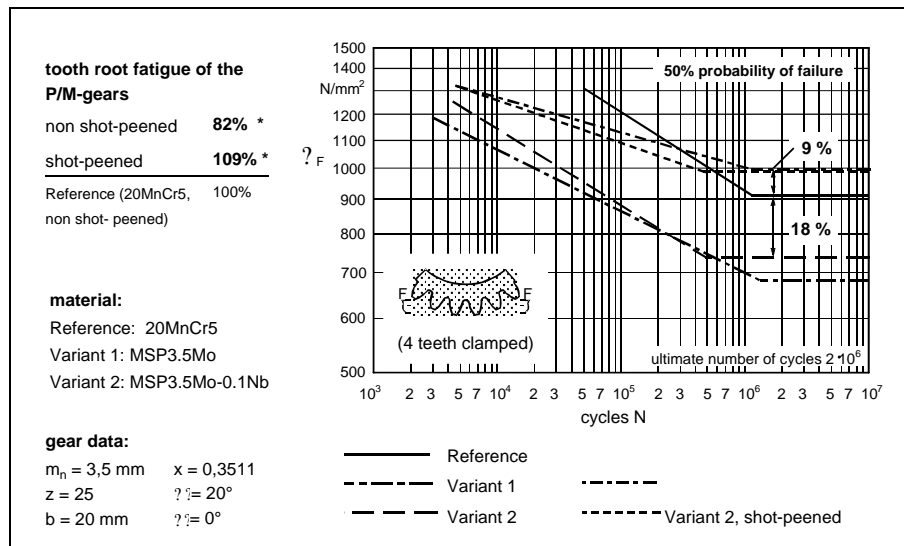


Fig. 11 Tooth root load-carrying capacity of the sintered variants compared to the reference variant [4]

6. Summary

The sintered steel MSP 3.5 Mo is characterised by its very high density of 7.5 g/cm³ as a result of sintering in the α -phase. The strength behaviour of this materials was initially examined in extensive materials science test programmes. By case hardening, the fatigue strength characteristics can be considerably improved, as carbon is introduced into the case, where it creates a martensitic microstructure. Special case hardening parameters must be selected for the material MSP 3.5 Mo because of its very high molybdenum content, in order to avoid the formation of special grain boundary carbides of the M₆C type, because those carbides impair toughness characteristics. The austenitising temperature selected must be above 1050°C to prevent the occurrence of special carbides. This was the purpose of the case hardening treatments.

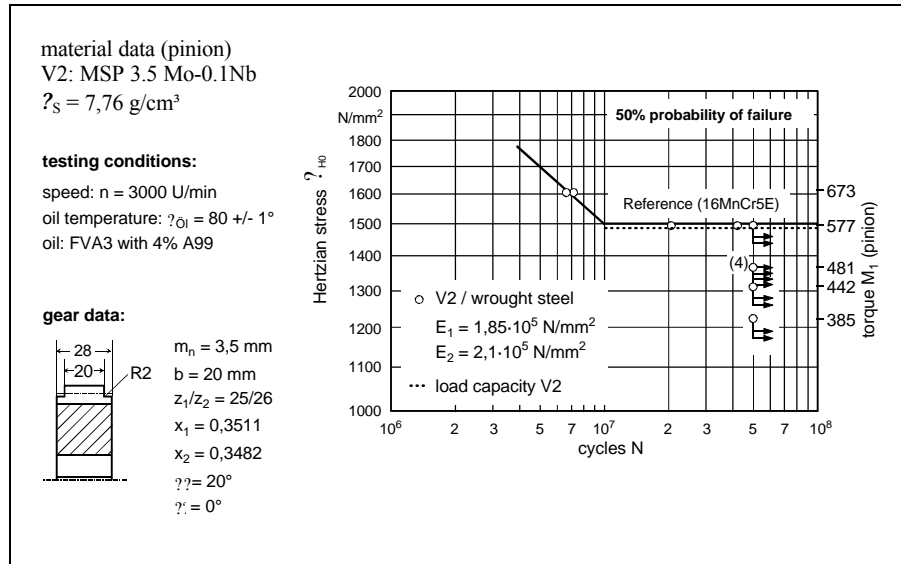


Fig. 12. Tooth flank load-carrying capacity of Variant 2 [4]

Pulsator tests were carried on sintered gears made from MSP 3.5 Mo in order to determine tooth-root load-carrying capacity. The tooth-root load-carrying capacity of the sintered gears was examined on gears with a module $m_n = 3.5 \text{ mm}$ in the unpeened and shot-peened states. The high-density PM gears attain roughly 80 % of the load-carrying capacity of the reference gear in the unpeened state. Following additional shot peening, the tooth-root load-carrying capacity of the PM gears is 9 % higher than that of the reference variant. Tooth-flank load-carrying capacity tests on Variant 2 (MSP3.5Mo-0.1Nb) PM gears show that fatigue strength values comparable to those for compact steel can be expected from the high-density sintered gears. The application of MSP 3.5 Mo with its high shrinkage is requesting a special process technology and process control in order to reach the required dimensional change behaviour.

Acknowledgement

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