

# **Diffusion-bonded Molybdenum Steel Powders for High Strength Applications**

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## **ABSTRACT**

New applications in the field of powder metallurgy require materials and process technologies which permit the economic production of high strength PM parts. High mechanical properties can be achieved by the use of pre-alloyed molybdenum steel powders. Direct sinter hardening of pre-alloyed molybdenum steel powders diffusion-bonded with nickel and copper in special furnaces with rapid cooling zones allows a martensitic microstructure to be produced.

The paper illustrates the mechanical properties of a pre-alloyed 1.5% molybdenum steel powder to which 2% copper and 4% nickel have been diffusion-bonded. Copper and nickel were diffusion-bonded to the base material to avoid segregation of press ready mixes and to ensure dimensional stability. The mechanical properties of pressed, sintered and tempered specimens made from press ready mixes based on the optimised molybdenum steel powder were evaluated at different carbon contents and at different sintered densities. Furthermore the microstructure of above mentioned specimens were evaluated to determine the effect of different cooling rates.

The optimised pre-alloyed molybdenum steel powder allows the manufacturing of PM parts with a tensile strength of more than 850 MPa by using normal sintering conditions in belt furnaces equipped with a rapid cooling zone.

## **INTRODUCTION**

In recent years, it has been recognized that dusts containing nickel constitute possible health hazard. This problem is leading to a considerable amount of legislation – affecting the production both of the powders and the PM parts – relating to the handling of premixed powders. Various alloying techniques have been developed to eliminate this problem. Well known are the diffusion-bonded Fe-Ni-Cu-Mo powder grades. Sintered materials of PM parts made from such powders are characterized by an inhomogeneous microstructure and tensile strength of 500 to 750 MPa [1]. The formation of Ni-rich dust can also be

eliminated by the use of prealloyed steel powders like Fe-Ni-Mo grades. The main advantages of prealloyed steel powders are the more effective utilisation of the alloying elements and the homogeneous microstructure.

In recent years another alloying technique has been developed to avoid the formation of dust and to avoid segregation of the alloying elements in premixes. The alloying elements, e.g. Cu and Ni, are binder treated to prevent Ni and Cu segregation and to improve dimensional stability. The resulting material properties are similar to diffusion bonded powder grades.

The demand for high strength sintered applications with high dimensional stability grew strongly during recent years. This resulted in the development of hybrid materials which allow the manufacturing of high strength applications by using sinter hardening. Sinter hardening enables the production of PM parts with high strength and apparent hardness at lower cost than conventional heat treatment. The sinter hardening process requires a base powder with enough hardenability to generate a high amount of martensite when the parts are cooled from sintering temperature. The powder grade ATOMET DB49 has been developed as suitable material for high strength applications with require high dimensional stability. This material is based on a 1.50% prealloyed Mo-steel powder to which 2.00% Cu and 4.00% Ni have been diffusion bonded. The benefit of this system is the combination of high strength and hardenability of prealloyed sinterhardening grades with the good compressibility of diffusion bonded or binder treated materials. The prealloyed Mo-steel powder has been selected as base material in order to distribute the heavy metal molybdenum homogeneously in the iron matrix, which cannot be obtained by admixing or diffusion-bonding molybdenum in standard sintering conditions [2].

The effect of the alloying techniques on the sintered material properties of such material system has been evaluated in a feasibility study. The nominal chemical composition as well as the alloying techniques used for each premix evaluated are given in Table I.

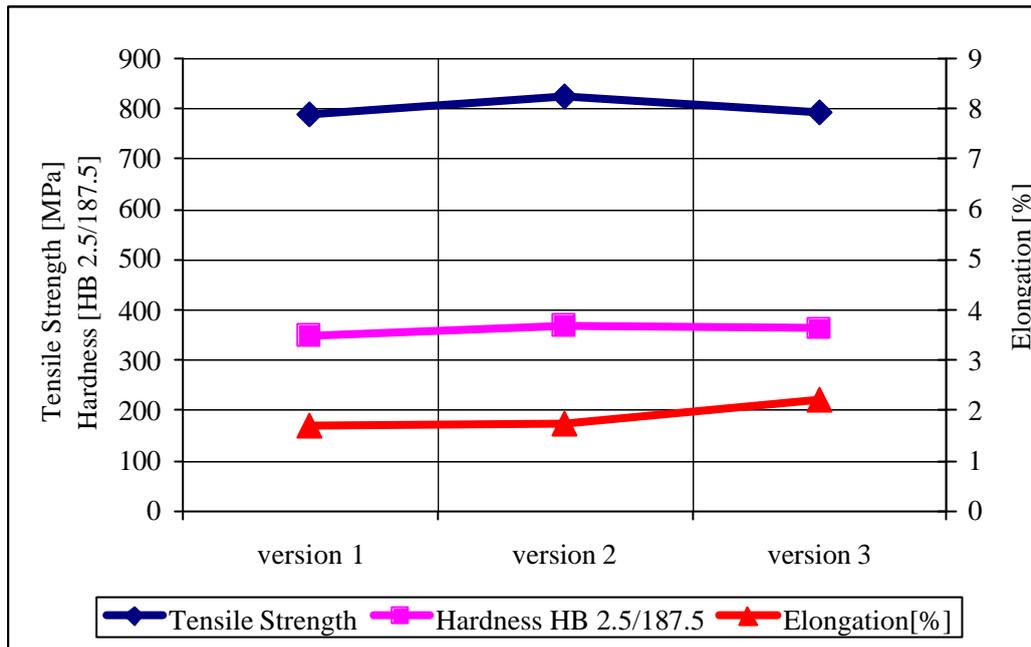
Table I Feasibility study: nominal composition and alloying techniques

Version	Mo, %	Ni, %	Cu, %	Graphite, %	Alloying technique
1	1.41	4.00	2.00	0.60	diffusion bonded
2	1.41	4.00	2.00	0.60	binder treated
3	1.41	4.00	2.00	0.60	plain mix

Note - Molybdenum was prealloyed in the base material for all versions

The feasibility study showed that the alloying technique has no significant effect on the material properties of the sintered part (figure I). To fulfil environmental regulations as well as to avoid segregations in mixes, however, it is strongly required to use mixes in which the alloying elements are diffusion-bonded or binder treated to the base material [3].

The objective of the study presented in this paper was the evaluation of the effect of various carbon contents and various tempering temperatures on the mechanical properties of the diffusion bonded material ATOMET DB49 (version 1 in table I).



Sintering conditions: 1120°C, 30min., 90%N<sub>2</sub> 10%H<sub>2</sub> , rapid cooled, tempered

Figure I Influence of alloying techniques on material properties (sinter hardened - tempered)

## **EXPERIMENTAL PROCEDURE**

Five mixes of the tested material (table II) were prepared with 0.80% wax and various graphite additions to reach combined carbon concentrations in the range of 0.15% to 0.95%.

Table II: nominal mix composition <sup>1)</sup>

Mix	Mo, %	Cu, %	Ni, %	Graphite, %	Wax, %
A	1.41	2.00	4.00	0.17	0.80
B	1.41	2.00	4.00	0,38	0.80
C	1.41	2.00	4.00	0,55	0.80
D	1.41	2.00	4.00	0,78	0.80
E	1.41	2.00	4.00	0,98	0.80

<sup>1)</sup> base powder: ATOMET 4901 (Fe-1.50Mo)

Ni and Cu were diffusion-bonded to the base powder. Graphite and wax were admixed

The mixes were compacted into MPA test bars (dog bones) at green densities of 6.70 g/cm<sup>3</sup>, 6.90 g/cm<sup>3</sup> and 7.10 g/cm<sup>3</sup>. The bars were then sintered in a conveyor belt furnace with convective cooling zone in 90% nitrogen base atmosphere for about 30 minutes at 1120°C. The cooling conditions were varied by changing the rotation speed of the fan between 20% and 80% of maximum value. Previous tests showed that a rotation speed of 80% results in a cooling rate of about 1.5°C to 2.0°C in the temperature range of 650° to 400°C. Tempering treatments were then carried out at 200°C, 250°C and 300°C for 60 minutes in pure nitrogen atmosphere. Apparent hardness and tensile properties were determined according to ISO standards. Microstructural characterisation was performed by optical microscopy.

## **RESULTS AND DISCUSSION**

The effect of the low cooling rate, the combined carbon content and the green density on the tensile strength and apparent hardness is shown in figure II.

The general trend in the as-sintered condition is a increase in tensile strength up to a maximum at a combined carbon level range of about 0.55% to 0.60%. The maximum tensile strength of 875 MPa in as-sintered condition was obtained with test bars pressed to a green density of 7.10 g/cm<sup>3</sup> at a combined carbon level of 0.55%. The tensile strength decreases drastically at combined carbon contents higher than 0.60%. Figure II shows also plots of the tensile strength after tempering. The tensile strength is slightly lowered after tempering up to a combined carbon concentration of about 0.55% to 0.66%. The tensile strength is significantly improved after tempering at combined carbon concentrations of more than 0.60%. The maximum tensile strength value is shifted to higher combined carbon levels in comparison to the as-sintered condition. The maximum tensile strength after tempering was obtained at combined carbon level of 0.75% The corresponding test bars were pressed to a green density of 7.10 g/cm<sup>3</sup> and tempered at 200°C for 60 minutes. In this particular case tempering treatment raise the tensile strength could be improved from 670 MPa to 870 MPa.

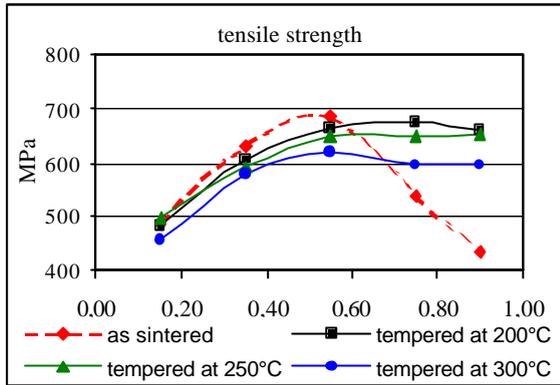
The maximum apparent hardness of 365 HB 2.5/187.5 in as-sintered condition was obtained at a combined carbon concentration of 0.75% with test bars pressed to a green density of 7.10 g/cm<sup>3</sup>. The apparent hardness decreases in as-sintered condition when the combined carbon level is increased from 0.75% to 0.95%. This is probably related to a higher amount of retained austenite in this material. This occurrence of retained austenite is favored when the carbon and other alloying elements concentration are increased [4]. Also, the high concentration of nickel in this alloy contributes to the retention of retained austenite in high carbon steels [5].

Tempering reduces the apparent hardness as shown in figure II. The maximum difference between the apparent hardness achieved in as-sintered condition and the values achieved after tempering was obtained at a combined carbon level of 0.75%. This is probably related to the larger amount of martensite produced which increases the softening effect due to increased amount of tempered martensite.

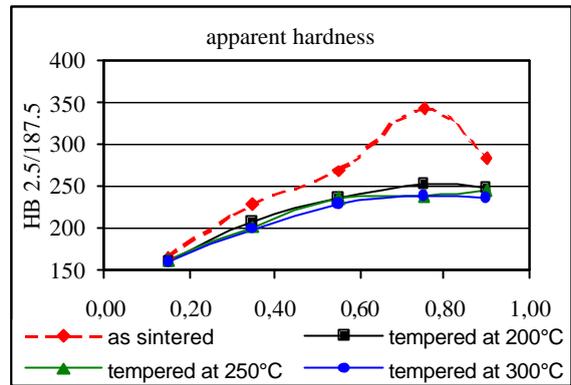
The effect of tempering temperature on apparent hardness of test bars tempered in the range from 200°C to 300°C is not significant. In all cases there is a significant decrease in apparent hardness compared to as-sintered condition.

Figure III illustrates the microstructure obtained with the test samples pressed to a green density of 7.10 g/cm<sup>3</sup> with combined carbon contents of 0.15%, 0.55% and 0.95% (20% fan speed). The microstructure of test bars in the as-sintered condition is composed of pearlite, bainite and even martensite at a combined carbon content of 0.55% and a low post-sintering cooling rate. At the higher combined carbon content of 0.95%, the microstructure is composed of plate martensite with retained austenite. This confirms the

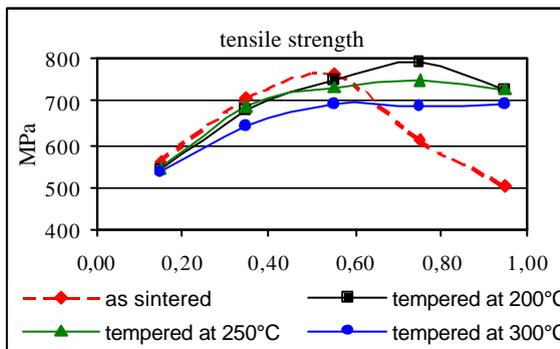
above mentioned observation regarding the lower apparent hardness at this combined carbon concentration.



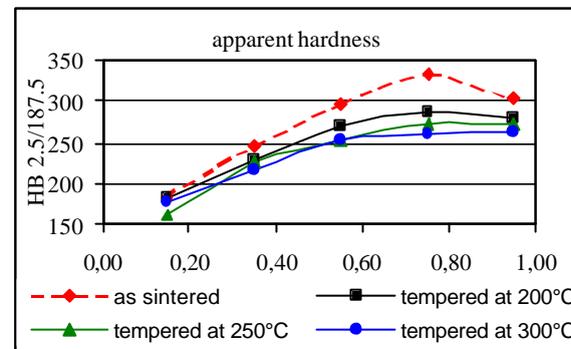
green density: 6.70 g/cm<sup>3</sup>



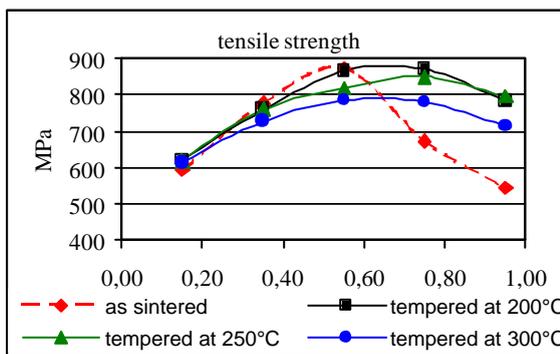
green density: 6.70 g/cm<sup>3</sup>



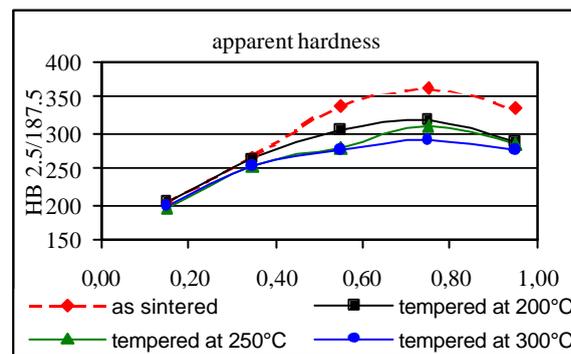
green density: 6.90 g/cm<sup>3</sup>



green density: 6.90 g/cm<sup>3</sup>



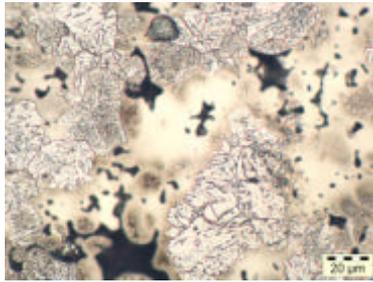
green density: 7.10 g/cm<sup>3</sup>



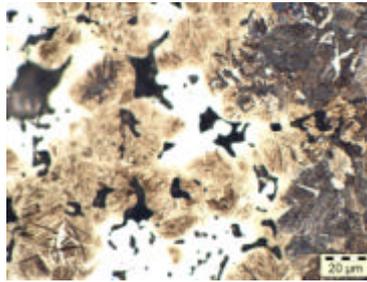
green density: 7.10 g/cm<sup>3</sup>

Figure II Evolution of tensile strength and apparent hardness with the combined carbon concentration for low post-sintering cooling rate (fan speed: 20%)

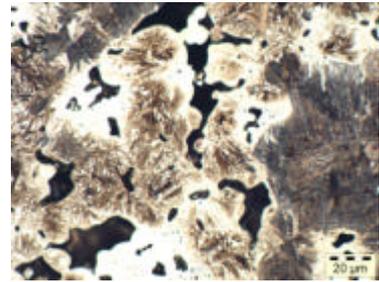
Tempering at 200°C, 250°C and 300°C has no significant effect on the microstructure of test bars pressed to a green density of 7.10 g/cm<sup>3</sup> with a combined carbon content below 0.55%. The microstructure of test bars with 0.95% combined carbon, however, is effected by tempering.



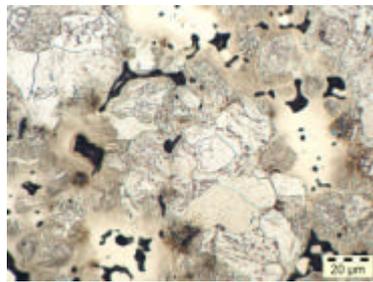
combined carbon: 0.15%  
as-sintered



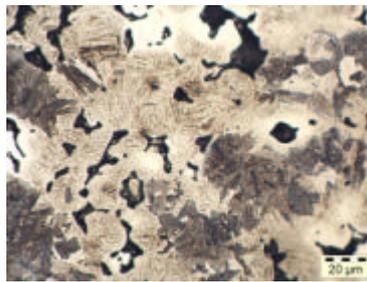
combined carbon: 0.55%  
as-sintered



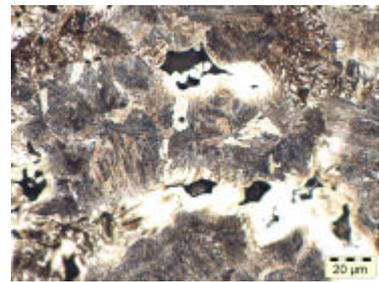
combined carbon: 0.95%  
as-sintered



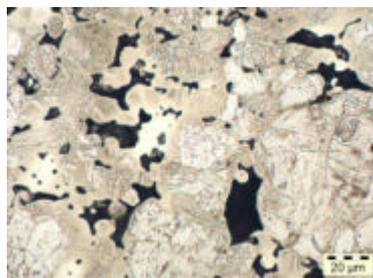
combined carbon: 0.15%  
tempered at 200°C/60 min/N<sub>2</sub>



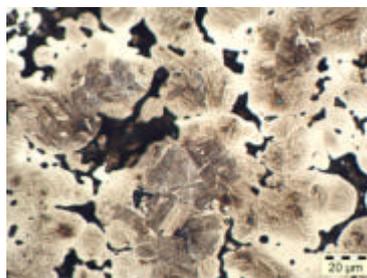
combined carbon: 0.55%  
tempered at 200°C/60 min/N<sub>2</sub>



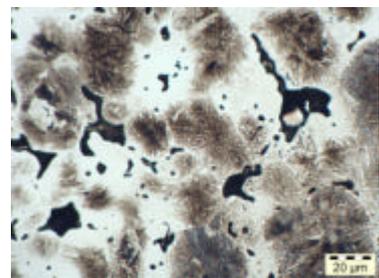
combined carbon: 0.95%  
tempered at 200°C/60 min/N<sub>2</sub>



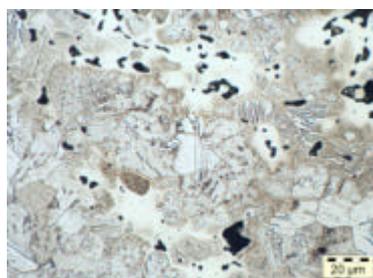
combined carbon: 0.15%  
tempered at 250°C/60 min/N<sub>2</sub>



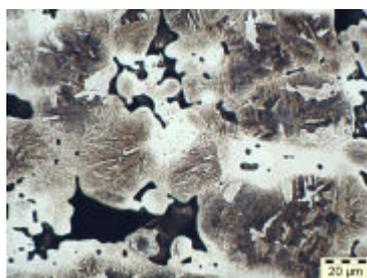
combined carbon: 0.55%  
tempered at 250°C/60 min/N<sub>2</sub>



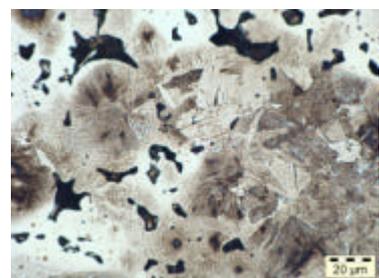
combined carbon: 0.95%  
tempered at 250°C/60 min/N<sub>2</sub>



combined carbon: 0.15%  
tempered at 300°C/60 min/N<sub>2</sub>



combined carbon: 0.55%  
tempered at 300°C/60 min/N<sub>2</sub>



combined carbon: 0.95%  
tempered at 300°C/60 min/N<sub>2</sub>

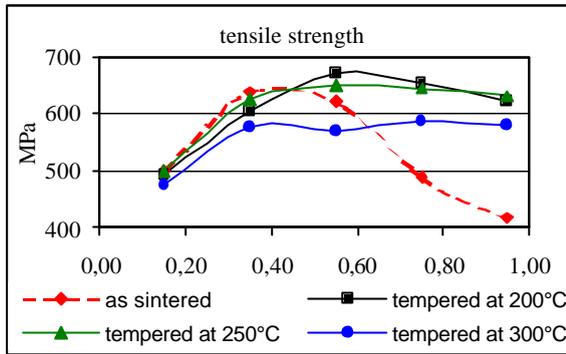
Figure III Micrographs of the material with the combined carbon concentrations for low post-sintering cooling rate (fan speed: 20%), green density: 7,10 g/cm<sup>3</sup>

The amount of retained austenite is slightly decreased after tempering at 200°C. Tempering at this temperature results in a more relaxed matrix which confirms the observation that the apparent hardness is lower and the tensile strength is higher in comparison to the as-sintered condition. The microstructure of test bars with 0.95% combined carbon content is composed of tempered martensite and several areas of pearlite with cementite at the grain boundaries. The amount of cementite at the grain boundaries is increased after tempering at 300°C. The retained austenite is almost fully transformed to martensite.

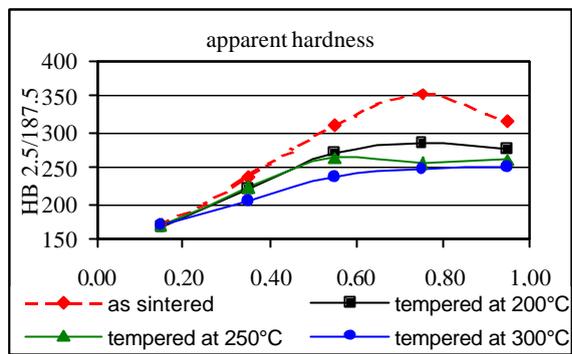
Figure IV shows the evolution of the tensile strength and apparent hardness of test bars cooled after sintering with a high cooling rate. In the as-sintered condition, the maximum tensile strength is reached at a combined carbon concentration range of 0.35 - 0.40%. In general, the maximum tensile strength of all test bars cooled after sintering with a high cooling rate is shifted to lower combined carbon levels in comparison to the tensile strength obtained with test bars cooled after sintering with a low cooling rate. The maximum tensile strength of 840 MPa in as-sintered condition was obtained with test bars pressed to a green density of 7.10 g/cm<sup>3</sup> with a combined carbon concentration of about 0.35 %. The maximum tensile strength obtained at high cooling rate is lower by almost 5% in comparison to the maximum tensile strength obtained with test bars cooled with lower cooling rate after sintering. The tensile strength at combined carbon concentrations up to 0.40%, however, is higher in comparison to the specimen with same combined carbon concentrations but cooled with lower cooling rates. This is probably related to the larger amount of martensite produced at the high cooling rate. The tensile strength drastically decreases at combined carbon contents higher than 0.40% which is related to the formation of retained austenite. The martensite finish temperature continuously decreases with higher combined carbon concentrations, e.g. to a temperature of -60°C at a combined carbon level of 0.80%. On the other hand the apparent density increases up to combined carbon content in the range of 0.75% to 0.80%. The maximum apparent hardness of 435 HB 2.5/187.5 in as-sintered condition was obtained with specimen pressed to a green density of 7.10 g/cm<sup>3</sup> with a combined carbon concentration of 0.75%. The apparent hardness decreases at higher combined carbon concentrations than 0.75% due to the higher amount of retained austenite. This behaviour was already observed at the specimens which have been cooled with low cooling rate after sintering. Tempering decreases the apparent hardness due to a relaxation of the lattice. The tensile strength is significantly improved by tempering at combined carbon levels higher than 0.50%.

Figure V illustrates the microstructure obtained with specimen pressed to a green density of 7.10 g/cm<sup>3</sup> with combined carbon contents of 0.15%, 0.55% and 0.95%. The microstructure of test bars in as-sintered condition with a combined carbon content of 0.55% is almost fully martensitic with few areas of retained austenite. A martensitic microstructure (plate martensite) with retained austenite was observed at the high combined carbon content of 0.95%. This explains the lower apparent hardness at this combined carbon level due to higher concentration of retained austenite in comparison to the apparent hardness of test bars with a combined carbon content of 0.75%. In general, the amount of martensite observed in the microstructure of fast cooled test bars is higher than the values obtained with specimen slow cooled after sintering. This confirms that the fan speed of 80% in the convective cooling zone of the conveyor belt furnace used is high enough to prevent the diffusion of carbon atoms and to form martensite during cooling.

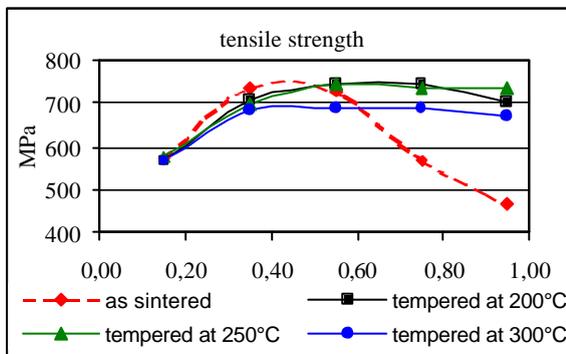
After tempering at 200°C the microstructure of test bars with combined carbon contents of 0.55% is composed of fully tempered martensite. The same microstructure was observed in specimens of the same combined carbon level but tempered at 250°C. The microstructure consists of cubic martensite and retained austenite at the higher combined carbon content of 0.95% after tempering at 200°C. The microstructure of specimen with combined carbon levels of 0.95% and tempered at 250°C is composed of almost fully cubic martensite with a few areas of retained austenite around Ni-rich zones. The microstructure of specimen with 0.55% combined carbon is composed of tempered martensitic structure and pearlitic islands after tempering at 300°C. Fully tempered martensite was observed at the higher combined carbon level of 0.95%.



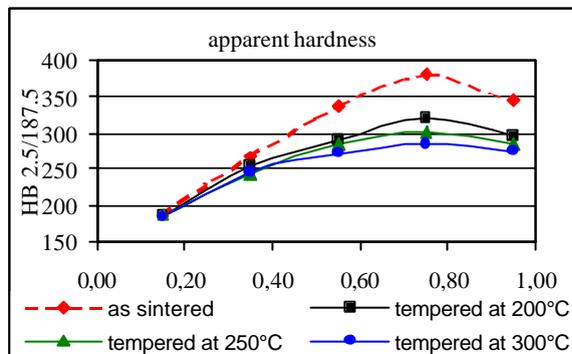
green density: 6.70 g/cm<sup>3</sup>



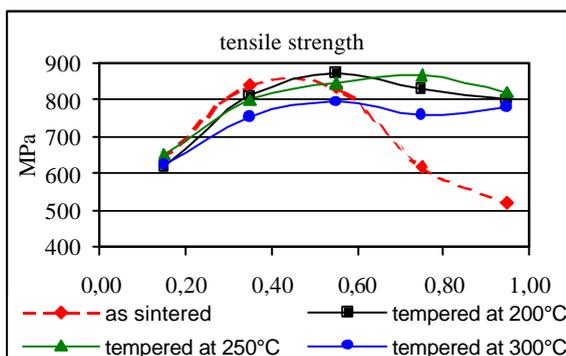
green density: 6.70 g/cm<sup>3</sup>



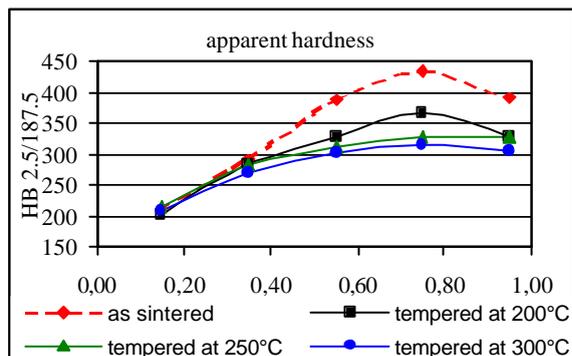
green density: 6.90 g/cm<sup>3</sup>



green density: 6.90 g/cm<sup>3</sup>

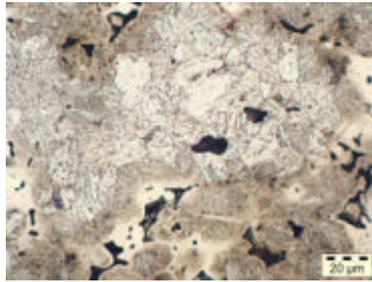


green density: 7.10 g/cm<sup>3</sup>

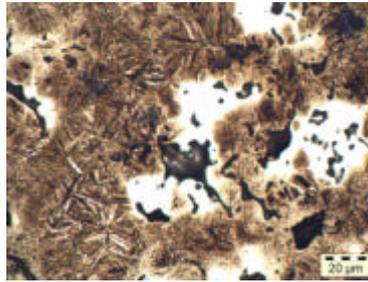


green density: 7.10 g/cm<sup>3</sup>

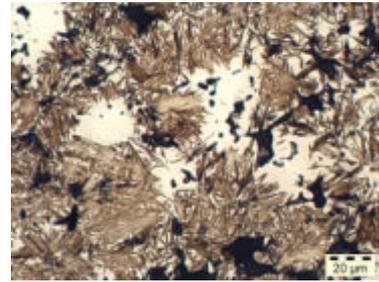
Figure IV Evolution of tensile strength and apparent hardness with the combined carbon concentration for high post-sintering cooling rate (fan speed: 80%)



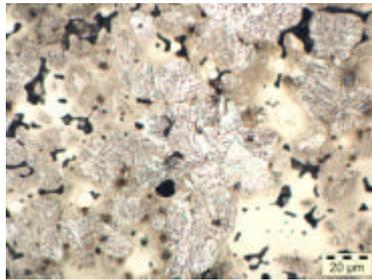
combined carbon: 0.15%  
as-sintered



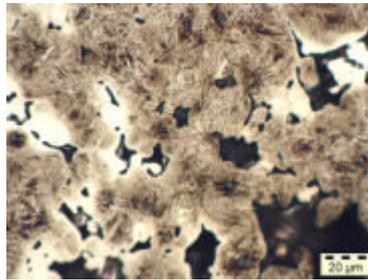
combined carbon: 0.55%  
as-sintered



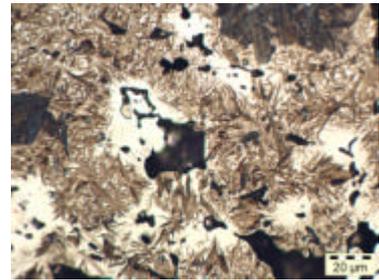
combined carbon: 0.95%  
as-sintered



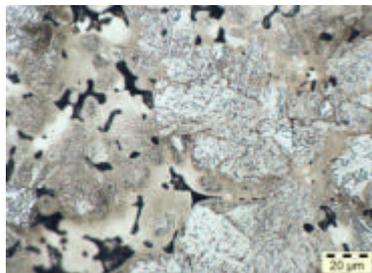
combined carbon: 0.15%  
tempered at 200°C/60 min/N<sub>2</sub>



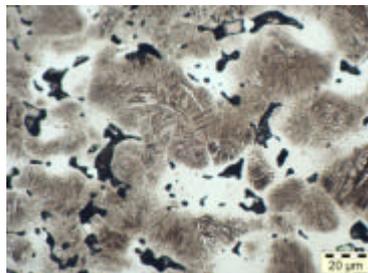
combined carbon: 0.55%  
tempered at 200°C/60 min/N<sub>2</sub>



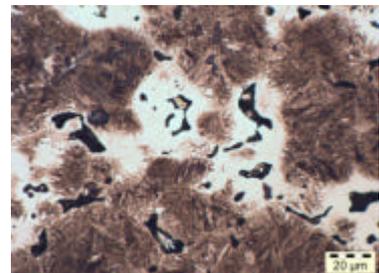
combined carbon: 0.95%  
tempered at 200°C/60 min/N<sub>2</sub>



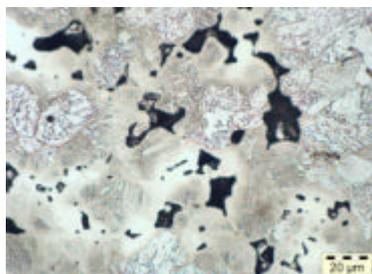
combined carbon: 0.15%  
tempered at 250°C/60 min/N<sub>2</sub>



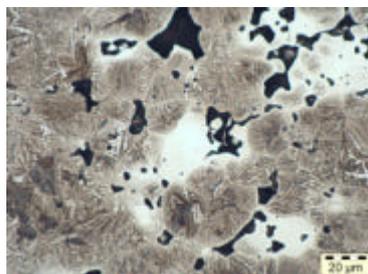
combined carbon: 0.55%  
tempered at 250°C/60 min/N<sub>2</sub>



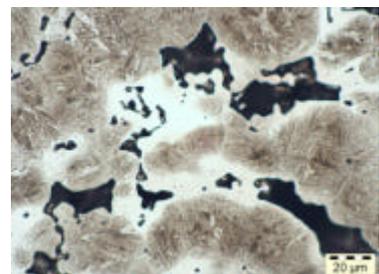
combined carbon: 0.95%  
tempered at 250°C/60 min/N<sub>2</sub>



combined carbon: 0.15%  
tempered at 300°C/60 min/N<sub>2</sub>



combined carbon: 0.55%  
tempered at 300°C/60 min/N<sub>2</sub>



combined carbon: 0.95%  
tempered at 300°C/60 min/N<sub>2</sub>

Figure V Micrographs of the material with the combined carbon concentrations for high post-sintering cooling rate (fan speed: 80%), green density: 7,10 g/cm<sup>3</sup>

## **CONCLUSION**

The paper discusses the mechanical properties of a pre-alloyed 1.5% molybdenum steel powder to which 2% copper and 4% nickel have been diffusion-bonded at different carbon contents and at different sintered densities. The microstructure of above mentioned specimens were evaluated to determine the effect of different cooling rates.

The optimised pre-alloyed molybdenum steel powder allows the manufacturing of PM parts with a tensile strength of more than 850 MPa by using normal sintering conditions in belt furnaces equipped with a rapid cooling zone without costly additional process steps like double pressing and double sintering.

A further step would be to determine the influence of cooling rate and also of tempering conditions on fatigue properties of the material.

## **ACKNOWLEDGEMENT**

Our sincere thanks go to Sinterstahl GmbH/Germany for its generous support regarding sintering of test bars.

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