PRE-ALLOYED CHROMIUM MATERIAL WITH CONSISTENT PROPERTIES FOR MEDIUM STRENGTH APPLICATIONS.

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Abstract - Chromium as an alloying element is of main interest due to its effect on hardenability. Compared to powder with nickel and molybdenum it is cost efficient and recycling causes no problem, which is the case for example with copper. In a pre-alloyed state the activity of chromium is low whereas the activity of chromium added in elemental form or as a master alloy is rather high, which enhances the possibility to use normal sintering conditions i.e. 1120°C, 90/10 N_2/H_2, 30 min. To prevent oxidation partial pressure of oxygen in the sintering atmosphere should be below $5*10^{-18}$ atm. when sintering chromium alloyed materials. A benefit from using a pre-alloyed powder with chromium for sintered parts is the enhanced dimensional tolerances. The paper describes a low alloyed powder with chromium as the major alloying element and comparison is made to Fe-Cu-C powder. The low amount of alloying element results in a total low cost for parts made thereof. The strength levels achieved with these two alloying systems are similar but the potential for close dimensional tolerances are substantially improved with the chromium alloyed powder.
KEYWORDS: PRE-ALLOYED Cr, PM, SINTERING CONDITIONS, MECHANICAL PROPERTIES

I. INTRODUCTION

Powder metallurgy has a strong growing market. Since most of the parts made by P/M are for the automotive industry cost is a major driving force. In development work for new grades not only cost but also performance is to be taken into account. In recent years new techniques/alloying systems have been developed in order to increase the ratio of performance and cost. Chromium as an alloying element is therefore of great interest due to low cost, even distribution of alloying elements and greater possibility to recycle material compared to Fe – Cu - C grades. A consequence of pre-alloyed grade compared to a plain mix is reduction of scattering in dimensional change which can be decreased to almost infinity if the graphite is bonded. This is one explanation why pre-alloyed grades is the most increasing grades.

In this paper a new water atomized pre-alloyed powder with 1.5% Cr + 0.2% Mo will be presented. Mechanical/physical properties and sintering behavior will be covered.

II. EXPERIMENT

In all evaluations base powder with chemical properties as shown in table 1 is used.

Table 1. Chemical composition (weight %).

Cr	Mo	C	O
1,5	0,2	<0,01	<0,25

Compressibility is evaluated according to ISO 3927-1985 and mechanical properties according to ISO 2740-1986.

Sintering is performed in a laboratory belt furnace at 1120°C for 30 minutes at temperature in 90/10 N_2/H_2. Hydrocarbon (methane) is used for carbon control and added in volume percent, defined by the graphite level in the mix. Oxygen probe is used for control of the partial pressure of oxygen. In all trials the oxygen probe is placed beside the belt in the middle of the sintering zone. Demand for successful sintering is a partial pressure of oxygen below $5*10^{-18}$ atm [1].

III. RESULT

Compressibility is presented in table 2. Evaluated are cold compacted specimens by die wall lubrication, mix with 0.8% H-Wax, 0.8% Zn-stearate and 0.6% Kenolube. For warm compaction, DENSMIX™ with 0.6% lubricant is used.

Table 2 Compressibility

Comp. press	Die wall	H-Wax	Zn-st	Kenolu-be	Densmix
(Mpa)	(g/cm^3)	(g/cm^3)	(g/cm^3)	(g/cm^3)	(g/cm^3)
400	6,55	6,59	6,61	6,59	6,64
600	7,04	6,99	7,02	7,04	7,10
800	7,32	7,17	7,21	7,24	7,33

Warm compaction is performed with powder temperature of 130°C and a die wall temperature of 150°C.

Sintered properties are evaluated for mixes with base powder Fe -1.5% Cr - 0.2% Mo at carbon levels in a range of 0.2 – 0.8%. In order to compare with iron – copper–carbon system, a mix with base powder ASC100.29, added 2% Cu-200 mesh, carbon in the same range is included in the investigation. As lubricant, H-wax is used in an amount of 0.8%. Specimens are compacted in a range of 400 to 800 MPa and sintered in randomly order.

In figure 1, tensile strength at different carbon levels compacted at 600 MPa is presented.

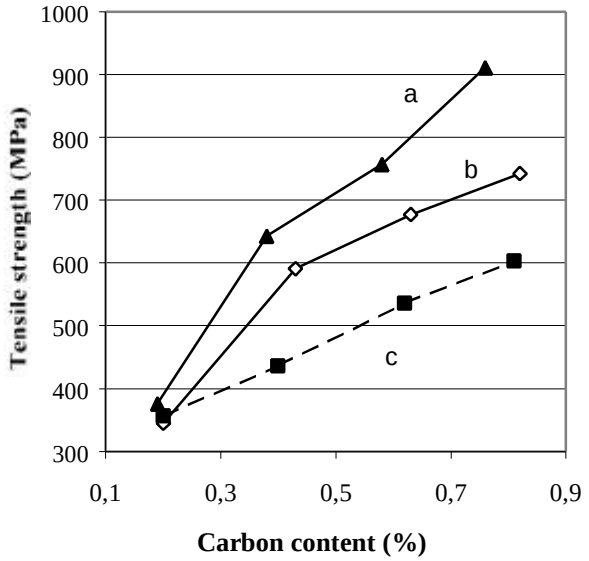


Figure 1. Tensile strength at different carbon levels, compacted at 600 MPa for Fe – 1.5% Cr – 0.2% Mo (a) warm compacted, (b) cold compacted and (c) Fe - 2% - Cu.

At 0.2% C the mechanical properties are in the same order. Hardness is here 100-115 HV10. Increase in properties at higher carbon content is a consequence due to transformation to bainite. By warm compaction the properties are further increased due to achieved higher density by this technique. The dimensional change is presented in figure 2. Compaction pressure is 600 MPa.

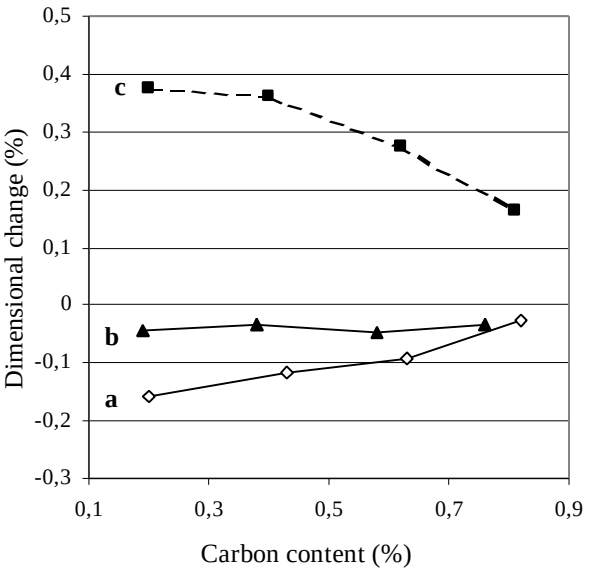


Figure 2. Dimensional change at different carbon levels for Fe – 1.5% Cr - 0.2Mo (a) cold compacted , (b) warm compacted and Fe – 2% Cu (c) cold compacted.

The iron – copper – carbon system has a higher dimensional change in the carbon range from 0.2 to 0.8 compared to Fe – 1.5% Cr – 0.2% Mo, warm and cold compacted. Warm compacted specimens have the same dimensional change throughout the carbon range.

Mechanical properties at different compaction pressure, cold compacted for Fe - 1.5% Cr - 0.2% - Mo with 0.43% and 0.83% C, are shown in table 3a (analysed at 600 MPa) and Fe - 2% Cu - 0.40% C and 0.81% C (analysed at 600 MPa) is shown in table 3b.

Table 3a. Mechanical properties, Fe - 1.5% Cr - 0.2% Mo with 0.43% and 0.83% C.

Comp. press	TS (MPa)		YS (MPa)		HV10		El. (%)	
	0,43	0,83	0,43	0,83	0,43	0,83	0,43	0,83
400	471	547	372	542	129	206	1,1	0,2
600	591	742	465	668	173	245	1,7	0,5
800	645	791	504	731	193	267	1,9	0,4

Table 3b. Mechanical properties, Fe – 2% Cu – 0.40% C and 0.81% C

Comp. press	TS (MPa)		YS (MPa)		HV10		El. (%)	
	0,40	0,81	0,40	0,81	0,40	0,81	0,40	0,81
400	346	506	258	403	110	167	2,2	1,2
600	436	603	311	458	128	185	3,6	1,7
800	472	644	334	481	139	206	3,8	1,8

If warm compaction is used the mechanical properties are further increased, table 4. Carbon analysed at 600 MPa.

Table 4. Mechanical properties for warm compacted Fe – 1.5% Cr - 0.2% Mo, 0.38% and 0.76% C

Comp. press	TS (MPa)		YS (MPa)		HV10		El. (%)	
	0,38	0,76	0,38	0,76	0,38	0,76	0,38	0,76
600	643	911	483	746	196	262	2,5	1,1
700	665	959	500	794	200	270	2,5	1,2
800	699	987	525	830	214	275	2,9	1

Investigation of the microstructure reveals a change from ferrite/pearlite structure to fully bainite structure at 0.4% C, figure 3a. Microstructure for Fe – 1.5% Cr – 0.2% Mo - 0.6% C consists of bainite and martensite, figure 3b.

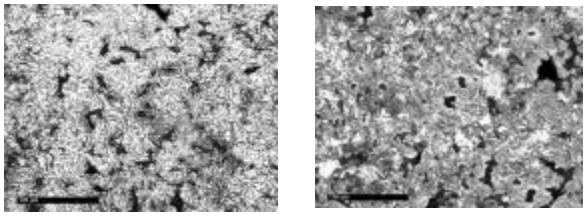


Figure 3. Microstructure for Fe – 1.5% Cr – 0.2% Mo (a) - 0.4% C and (b) - 0.6% C,

Control of sintering atmosphere is important for chromium containing materials. From the Richardsson-Ellingham diagram oxidation of chromium (1120°C) starts at ~$1*10^{19}$. In this case the activity of chromium is 1. In pre-alloyed state the activity at low amount of chromium could be set equal to the weight percent of chromium. This leads to oxidation if the partial pressure of oxygen is above $5*10^{-18}$ atm, stated by experimental work [1]. If no hydrocarbon is added to the atmosphere and graphite is present in the mix, formation of carbon monoxide starts to form at higher partial pressure of oxygen. Break point for oxidation can be detected, in this case the samples are quenched after time at sintering temperature [1]. If the partial pressure of oxygen is below $5*10^{-18}$ atm. some decarburization occurs. Normal decarburization is 0.04 to 0.09% [2] in this case. The decarburization is throughout the material. The amount of chromium for this new material is 1.5% to be compared with values for 3% Cr, presented above in this section. Oxidation is therefore to appear at slightly higher partial pressure of oxygen due to lower activity of chromium. In figure 4 decarburization and oxidation for Fe – 1.5% Cr - 0.20% Mo - 0.2% C at different partial pressure of oxygen is presented. In figure 5 the behaviour for Fe – 1.5% Cr - 0.25% Mo - 0.6% C at different partial pressure of oxygen is shown. The experiment is performed in a laboratory belt furnace at 1120°C for 30 minutes at temperature. The lowest partial pressure of oxygen is reached by use of dissociated ammonia, thereafter in 90/10 N_2/H_2 the final two evaluated partial pressures of oxygen are done by addition of moisture to the atmosphere. A defined volume of sintering gas mixture is passing through the moisturising equipment.

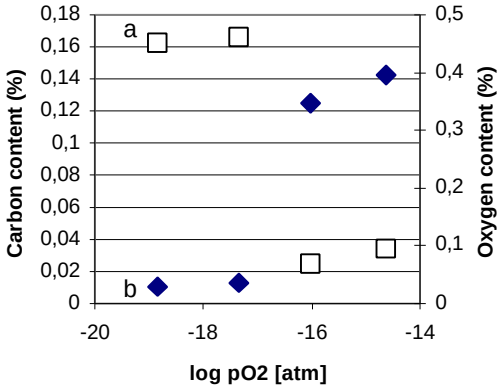


Figure 4. (a) Decarburisation and (b) oxidation of Fe – 1.5% Cr-0.2% Mo-0.2% C at different partial pressure of oxygen.

Amount of oxygen in the moistured atmosphere is obtained by temperature control in a water batch. No hydrocarbon is added to the sintering atmosphere.

At a partial pressure of $4*10^{-18}$ atm (-17,36) there is no decarburisation, excluded the one that appears due to reduction of chromium oxides. At $9*10^{-17}$ atm (-16,04), partial pressure of oxygen for the mix of 0.2% C all carbon has formed carbon monoxid and oxidation has occurred. Result for 0.6% C mix reveals at $9*10^{-17}$ atm that the decarburisation is high and the oxidation occurs. Analysed carbon and oxygen are as mean values for the cross section of the specimens.

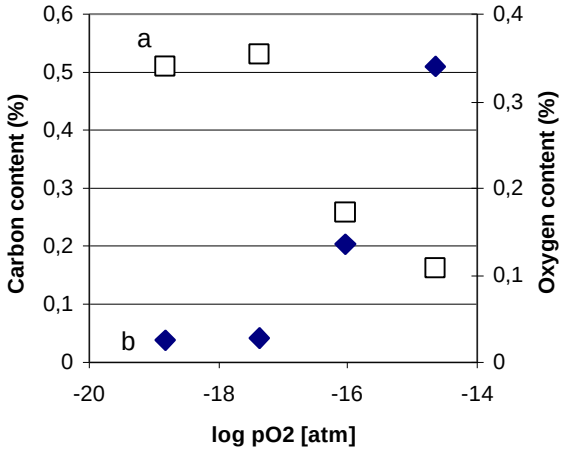


Figure 5. (a) Decarburisation and (b) oxidationn of Fe – 1.5% Cr-0.2% Mo-0.6% C at different partial pressures of oxygen.

Mechanical property, tensile strength obtained from these sintering trials, figure 4 and 5 are shown in figure 6.

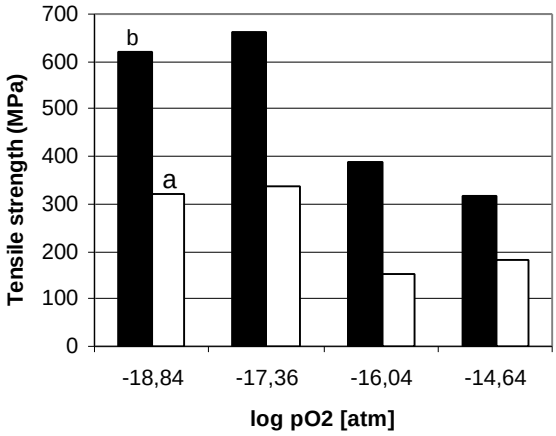


Figure 6 Tensile strength for Fe – 1.5% Cr - 0.2% Mo - (a) 0.2 and (b) 0.6% C.

Microstructure reveals that there exists a carbon gradient from the surface into the centre of the test piece. At the surface the microstructure is completely ferritic. Transformation into bainite, pearlite and martensite appears at different distance depending on carbon content and sintering conditions. Oxides are visual in the ferritic boarder.

IV. DISCUSSION

Compressibility for pre-alloyed grades is, due to the solid strengthening effect from the alloying elements, lower compared to mixed or partial pre-alloyed grades. In table 2 the compressibility is shown for the new water atomised pre-alloyed grade. Compared to the iron-copper (2%) – carbon system there is a difference of ~0.14 g/cm^3 in green density and after sintering ~0.08g/ cm^3. This is explained by the dimensional change, figure 2. Response in mechanical properties at the same compaction pressure is significant, figure 2 and table 3 and 4. Explanation for this is the transition from ferrite/pearlite/bainite microstructure to bainite at 0.4% C and formation of martensite at carbon levels of 0.6. This is stated by the selected chemical composition of the base powder. In table 3a and 3b comparison between the two systems shows, at 600 MPa, that approximately the same levels in mechanical properties are achieved for Fe – 1.5% Cr – 0.2% Mo - 0.41% C compared to Fe -2% Cu – 0.81% C. The elongation is 1.7% for both systems. Noteworthy is that lower compaction pressure is needed in order to achieve equal properties. Among factors that influence the dimensional tolerance in the as sintered state is content of graphite and alloying methods [3]. Combining the effect from pre-alloyed alloying elements and reduction in graphite amount with the fact that the dimensional change (figure 2) is closer to zero for the Fe – 1.5% Cr – 0-2% Mo system, closer tolerances can be achieved for this new material compared to the conventional Iron –Copper – Carbon system. By adopting the warm compaction technique dimensional change is the same throughout the investigated carbon range. Warm compaction is beneficial for the mechanical properties, figure 2. Higher density level is achieved with this technique, table 2. Warm compaction is here in the same order as die wall lubrication. Warm compacted specimens at 800 MPa with 0.76% C have a tensile strength of 987 MPa and a yield strength of 830 MPa. The elongation is in this case 1%. These are very high values in the as sintered condition.

Control of sintering atmosphere in order to prevent decarburisation and oxidation is important for all P/M grades. For chromium containing materials a partial pressure of oxygen at 1120°C of $5*10^{-18}$ atm or lower is a demand to ensure no influence from decarburisation or oxidation from the atmosphere. This ends up in that endo gas cannot be used for sintering of these materials. Mix of nitrogen and hydrogen is preferable. At this partial pressure it is possible to reduce chromium oxides. This leads to a slight decarburisation if no hydrocarbon is added to the sintering atmosphere or correction is made in the graphite addition in order to obtain expected carbon level. Indication for this can be seen in figure 4 and 5 at log $p0_2$ lower than –17,36. At higher partial pressure of oxygen decarburisation occurs and oxidation is also a case. Mechanical properties achieved in these not suitable sintering atmospheres reveal a large decrease. This is due to that the mean carbon content of the cross section is decreased. Carbon gradient exists from the surface to the centre.

V. CONCLUSION

- New water atomised pre-alloyed material with a chemical composition of Fe – 1.5% Cr – 0.2% Mo matches the Iron - 2% Copper – Carbon throughout the carbon range of 0.2 to 0.8%.
- Transformation from ferrite, pearlite and bainite at 0.2% C to complete bainite structure at 0.4% C increases the mechanical properties significant.
- Very high mechanical properties in the as sintered condition can be achieved by warm compaction of mix with 0.8% C.
- Sintering of Fe – 1.5% Cr - 0.2% Mo is to be done in an atmosphere with a partial pressure of oxygen lower than $5*10^{-18}$ atm at 1120°C.
- Addition of hydrocarbon to the sintering atmosphere or graphite addition in order to correct the decarburisation which occurs throughout the material due to reduction of chromium oxides is recommended.

V. REFERENCES

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