SYNTHESIS REPORT

CONTRACT No : BREU.0439,

PROPOSAL N° : BE.4028

TITLE : COMPOSITE POWDER METALLURGY MATERIAL FOR OPERATION UNDER POOR/NON LUBRICATING CONDITIONS FOR HEAVY DUTY DIESEL ENGINES

PROJECT COORDINATOR : SINTERTECH

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3. SINTERMETALLWERK KREBSÖGE GmbH (SMK)
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5. HOGANAS AB
6. COLDSTREAM SA
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STARTING DATE : 01/11/91 **DURATION :48 MONTHS**

1. INTRODUCTION

The aims of this project were :

- first, to develop new hard phase / solid lubricant / metal matrix composite materials by powder metallurgy,
- to use these materials (expected to have good dry friction properties) for the elaboration of several highly stressed components in heavy duty diesel engines with no / poor lubrication in order to reduce the toxicity of engine exhaust fumes.

Three components were initially emphasized : valve seat, valve guide and rocker arm. Different matrix materials were proposed in the project. mainly high speed steel material (HSS) and more classical iron bases. Production of the powders, compatibility studies between matrix and additions, compaction, sintering and mechanical analyses were checked in order to select promising materials. The best one were then submitted to friction screening tests to chose the final material(s) to be used for the realization of each component. A final engine. test will be made to establish their performance, a reduction of the oil consumption being waited.

2. POWDER ELABORATION

In the first part of the project HÖGANÄS AB, had to produce powders using an, established 'economic process. The technical approach was to develop powders in a range of sizes and alloy compositions. The project plan proposed powders with maximum particle sizes 10, 50 and 150 pm. Some material compositions suggested were Fe+1.5Cr, Fe+12.5Cr, Fe+18Cr+10Ni (SS), Ni+xCr and Stellite. In the project plan it was noted that the powders should not be to expansive and therefore the produced materials were to be low alloyed and water atomised. To get a finer particle size the powders have been sieved, rather than in this stage of the project developing new atomisation techniques and routines. Fe+ 1.5Cr was atomized but the particle size and shape was wrong since the alloy composition is not suitable for atomization. It was decided to use a material in production today, Astaloy Mo. This powder was sieved to get finer powder, X<75 µm Astaloy "Me. The two powders (standard and fine) were mixed with Fe_3P to get Astaloy PMo and X<75 µm Astaloy PMo. Fe+12.5Cr alloy is very difficult to sinter because of the high Cr content and was therefore cancelled. The M3/2, Astaloy Mo and Astaloy PMo are standard water atomized products of Höganäs AB. Al_2O_3, TiC, TiC/N, Cr_20_3 are hard phases that could be used in the matrix material. Cr_20_3 is not inert and WOWI be dissolved in the matrix, Al_2O_3 is too inert and has no interaction or bonding to the Astaloy matrix. TiC has better sintering properties than TiC/N and NbC have very good sintering properties and interaction with the M3/2 matrix, Al_2O_3-TiC/N-Cr_2O_3 hard phases have been cancelled for the time being. Concerning the solid lubricant, CaF_2 and mainly MnS were studied.

Compatibility of metal/ceramic/lubricant have been studied. H ÖGANÄS has made preliminary tests to select some systems using nettability studies, then University of Bradford (UOB) focused on high speed steel (HSS) based materials while AMES studied more classical iron based materials (Astaloy Mo, . ..).

2-a)- M 312 matrix :

Sintered specimens were subjected to thorough examination by X-ray dispersive analysis (EDA), back-scattered electron image contrast (BEI) and X-ray diffraction were used to aid the identification of phases present. A wide range of sintering temperatures was checked to study the different compatibilities.

Major changes occurred to the basic microstructure of the M 3/2 high speed steel matrix as a result of introducing either ceramic or solid lubricant particles, especially for alloys containing TiC and the combination of TiC/MnS particles. The addition of titanium carbide (TiC) changes the relative proportions of M_6C and MC carbides, M_6C carbides progressively disappeared from the microstructure, MC type carbides ' replaced them. At higher sintering temperatures, the replacement of M_6C is more noticeable. Energy dispersive analysis of this MC carbide phase also confirmed the existence of essentially different MC carbides at different sintering temperatures. Quantitative image analysis also indicated significant changes . to the size and volume fraction of the TiC particles retained by the microstructure after sintering at successively higher temperatures.

Niobium carbide additions to the M 3/2 HSS resulted in the formation of' large carbide agglomerates and the presence of carbide clusters/networks in the sintered structure. These clusters originated from the NbC particles addition but had undergone considerable change in composition as a result of the sintering process. Changes to the steel matrix were less pronounced for the NbC containing composites than were shown for the TiC type composites. No evidence of preferential replacement of the M_6C matrix carbide phase by niobium rich MC carbides in the steel matrix was found.

Less pronounced changes occurred to the microstructure of the M3/2 HSS when either of the solid lubricants MnS or CaF_2 were individually introduced into the sintered material. No evidence was found for any diffusional layers or of any new phase formation at the solid lubricant/HSS interface. Energy dispersive analysis also confirmed that little chemical interaction between either MnS or CaF_2 and molybdenum and chromium into the MnS particles. Despite the apparent lack of reaction between the steel and either of the solid lubricants, noticeable changes (quantified by image analysis) to the size (growth) and shape (rounding) of both MnS and CaF_2 were produced by sintering at high temperatures.

Composites containing both TiC and CaF_2 additions produced similar microstructure to those found in the M 3/2 + TiC composites ; the major effect being the shift in carbide population already described for the latter composite ; the CaF_2 showed no reaction other than to undergo the coarsening already described. This was not true of composites containing both TiC and MnS, which formed a reaction product, $Ti_4C_2S_2$ on sintering at high temperatures (above 1290°C). However, an optimum microstructure was achieved at a sintering temperature below that at which the carbosulphide formed. Sintering of the composite M 3/2 + NbC + MnS did not produce a similar reaction product ; other microstructural changes such as MC carbide composition variation with temperature. NbC and CaF_2 did not react together when sintered with the high speed steel but again the usual compositional changes to the Nb-rich carbide with temperature were observed.

2-b)- Classical iron based matrix :

TiC is not compatible only with pure H_2 atmosphere and it is with Endogas, N_2/20 % NH_3 D.A and N_2 / 5 % H_2 atmospheres. Moreover, the TiC does not react with MnS and reacts with the matrix, showing high diffusion between them. No compatibility problems were found between MnS, the sintering atmosphere and AsMo matrix. On the contrary, Astaloy PMo has to be sintered with N_2/20 % NH_3 D.A and N_2/ 5 % H_2 atmospheres.

2-c)- Study of Mechanical alloying of fine powder blends

The effects of attrition and ball milling were studied on 3 different types of HSS powders, namely fine gas atomised (25 pm), unannealed water atomised (500 µm) and commercial soft annealed water, atomised powder. The powders were milled in a laboratory attritor and a ball mill and the effects of milling parameters such as ball size, milling speed and powder load on particle shape and particle size distribution were investigated.

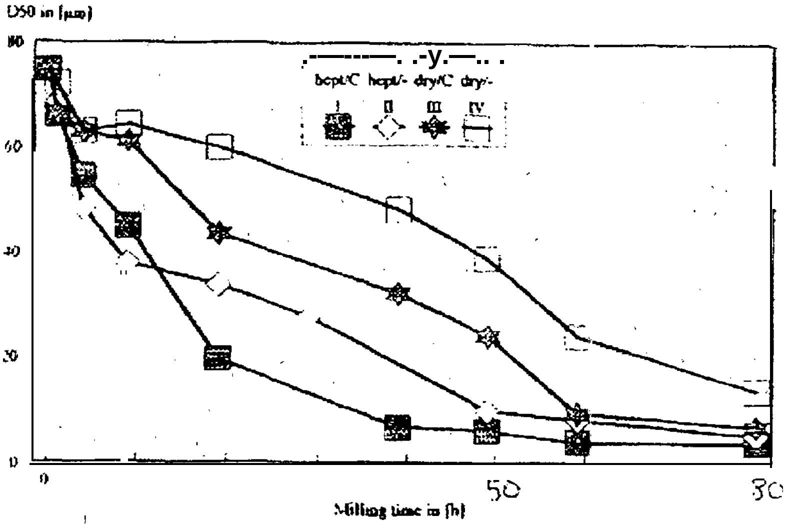
The HSS powder particles turned out to be remarkably ductile in attrition milling, even. the unannealed powder. After several hours milling time the powders became flaky regardless of the initial particle shape. Flaky powders are, extremely difficult to handle in powder metallurgy. and are usually avoided. Attritor milling is therefore not a suitable method to prepare these powders.

As far as Mechanical alloying is concerned, Höganäs AB has studied a base material with 10%NbC and Fe+10% Mo+ 0.2%B more closely. This material was chosen because it sintered very well at 1150°C with a transient liquid phase. The milling conditions were:

35% filled container
10%Cr_2 => 440g powder
4.4 kg 100C6 balls
Mill diameter: 0.195m
Mill speed :88 rpm.
Pressing :600 MPa =>66.87% (Green Density)

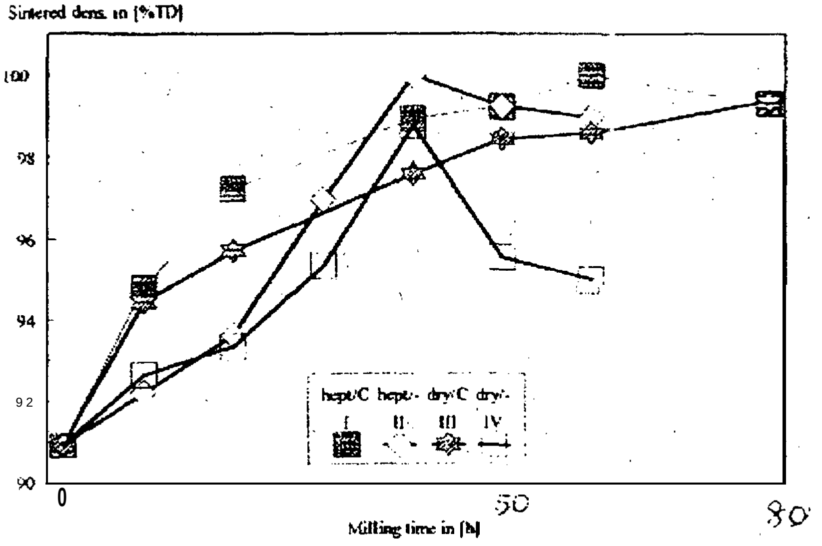
Sintered density independently of green density
Consolidation : Furnace
Hereaus 1150°C, 60 min (Sintering time)
Heating rate: 80 °K/min, cooling: 42 °K/min
cooling is fluxing Hydrogen+ 2%methane
(dew point -25°C, fluxing)

For reasons of comparison to other studies running at Höganäs AB, a charge ratio of 10: 1 is kept. With an estimated average apparent density of about 2 g/cm3 of the powder filling a fractional interstitial powder filling of U =0.6 is obtained. The mill operates with the same fractional' speed N = 0.70 for both charge types. This means in case of wet milling most of the balls are cascading in the drum and only a small, fraction is lifted to the top. Thus, the time between collision events is longer than in the optimal case. This lengthens the time necessary for mechanical alloying. As a consequence, shorter milling times in case of wet milling than determined in 'this study can be expected if a mill with higher speed or ball lifters inside the containers is employed.



Particle size (D50) versus milling time, 88 rpm, milled with and without heptane and carbon.

Heptane and carbon both act as a lubricant in the milling process, i.e. reducing the rewelding of the fracture materials. The heptane has a stronger influence on the particle size reduction both with and without carbon. The particle size reduces faster when milling in heptane than dry. With carbon the reduction is even faster. The welding predominant stage (5-10h) can be seen clearly in the dry milled powder. The steady state stage when there is an equilibrium between fracture and welding is reached after 40h for the heptane/carbon conditions and after more than 80h for the dry condition. In this steady state period the internal refinement is increased while the particle size is kept constant. A carbon addition promotes an increase of the particles specific surfaces. There are two reasons for this behaviour. The specific surface increases with decreasing particle size. But on the other hand the specific surface area for the powders milled with carbon is generally larger in the condition without carbon. This can be explained by the fact that carbon promotes disc like particles with a higher specific surface area than spherical particles of the same size.



Sintered density of Fe-10%Mo-10vol/o-1.4% C-0.2%B sintered at 1150°C

The sintered density is significantly dependent on the milling conditions and milling time. The milling time required for maximum hardness mrresponds well with the milting time for maximum density. The oxygen level of the powders is relative to the specific surface of the powder. There is no relation between oxygen levels of powders milled in different atmospheres. The influence of the milling conditions on the nitrogen amount in the powder is completely different. In case of dry milling the nitrogen content is strongly. increased with the milling time while in case of wet milling the increase is much smaller.

2-d)- Preparation of powder mixes and granulation for compacting

Mixtures do not flow even when using coarse powder. The aim of this step is to granulate the mixes in order to manage fine grain size powder and to obtain powder which can flow. Numerous tests have been carried out in a first step by Sintertech. The only good results were obtained by using dry granulation following a technique belonging to CIME-BOCUZE (a former PECHINEY Group company). All the properties are improved with the granulated mix and for a grain size larger than 160, pm, all the powders flow. But problems to have access to the know-how of CIME-BOCUZE have led us to find another granulation facilities. HOGANAS proposed then to be in charge of these new tests. They made experiments with spray drying, freeze granulation and granulation in a mixer of fine powders. Spray drying was made in HOGANAS equipment. The solvent and binder' was water and polyvinylalcohol. Freeze granulation was done at the Swedish ceramic 'institutes, the same solution binder system was used in this ' process. A slurry is sprayed- into liquid nitrogen, the frozen spray is then freeze dried in a vacuum container. Granulation can be done in any mixer, : Niro mixer was used. The binder was again polyvinylalcohol. The two first methods result in spherical powders with flow but with low AD. Flow was obtained and a higher AD for the powder granulated in the mixer.

These experiments show that" it is possible to granulate powders with fine alloy elements. The powder, properties are improved considerably when granulating. The conventional mix with no flow is very difficult to process since the flow and apparent density is poor. The granulated material is much easier to , process because the flow and apparent density are in the range of normal materials. It was decided for the following of the project that the mixes delivered by Höganäs to the others partners will be granulated unless for specific studies (for example ball milling on HSS).

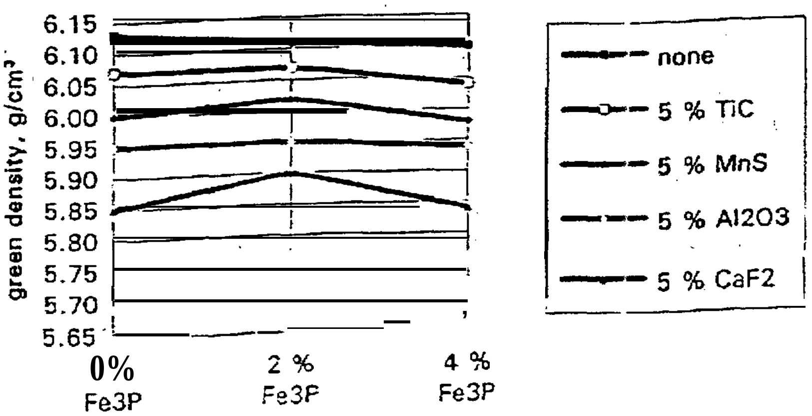
3- PROCESS PROPERTIES

3-a)- Compaction :

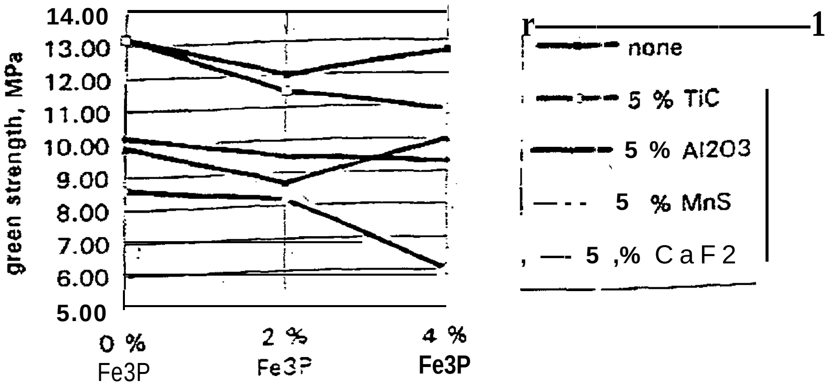
SMK worked on a variety' of 15 different powder compositions, mainly based on M 3/2 HSS materials. The first experiments concerning compaction behaviour were conducted using pure high speed steel powder and additions of only one of the other components to evaluate the influence on green density and green strength. MPA bars were compacted from the powder mixtures on a hydraulic press. The compacting pressure was 700 Mpa. Fig. 1 shows the green densities of the MPA bars. The non-metallic additives reduced the green density to a varying extent which could partially be attributed to the different theoretical densities of these additives themselves which are lower than the density of high speed steel powder. A secondary effect is given by the different grain sizes and grain-size distributions 'respectively. The addition of 2% of Fe_3P tended to increase the green density slightly because this powder is very fine and could fill the gaps between the coarser high speed steel powder particles. With an amount of 4% Fe_3P the green density decreased due to the lower theoretical density of the Fe_3P powder.

The green strength is negatively affected by all additives in a more or less pronounced way. The lowest green strength was found with CaF_2 additions. However, due to the high green strength of water atomised high speed steel powders even the lowest green strength was still sufficient for handling the green parts. The influence of the amount of non-metallic additives on green strength is shown in Fig. 2.

Additional mixtures containing sintering aids and/or other, non-metallic additives were prepared for sintering due to the expected low sintered densities of materials (table 3). ,



Fiq. 1 : Effect of additions to M3/2 powder on green densities



Fiq. 2: Effect of additions to M3/2 powder on green strength

N“	1B	20	3B	46	56
Material composition	100% M3/2	95% M3/2 5% Tii 1	95% M3/2 5% MnS	95% M3/2 5% CaF_2	95% M312 5% Al_2O_3
No	6B	7B	8B	96	106
Material composition	98% M3/2 2% Fe_3P	93% M3/2 5% TiC 1 2% Fe_3P	93% M3/2 5% MnS 2 % Fe_3P	93% M3/2 5% CaF_2 2% Fe_3P	93% M3/2 5?40 Al_2O_3 2% Fe_3P
No	11B	126	13B	14B	15B
Material composition	96% M3/2 4% Fe_3P	91% M3/2 5% TiC 1 2% Fe_3P	91% M3/2 5% MnS 2% Fe_3P	91% M3/2 5% CaF_2 2% Fe_3P	91 % M3/2 5% Al_2O_3 2% Fe_3P

Table 3: Composition of materials 1 B-15B

AMES worked on a variety of Astaloy Mo ‘base composites. Mixtures were compacted in order to evaluate their properties, like compressibility. spring-back, specific ejection force, green strength and suitable compacting pressure. Mixtures can not be compacted without wax, but they can by using only an 0.40A. Astaloy Mo base mixtures have similar compressibility than Astaloy PMo base mixtures and higher than Cold PMo. The admixed graphite decreases compressibility a little, while copper has the opposite effect. Mixtures of Astaloy < 75 µm have lower impressibility than the ones with coarse powder, and they produce some cracks in compacts. The TiC deweases compressibility. On the contrary, the MnS content does not affect compressibility understood as relative density- If its particle size is too big, some cracks appear again in compacts. The compressibility can be increased using MnX rather than MnS. Finally, the Mechanical Alloying mixtures have very bad compressibility, producing a large quantity of, cracks (excessive spring-back). Granulation seems to be a good mixing process for obtaining mixtures with good compressibility and high green "strength.

SINTERTECH worked on same bases as AMES and also on stainless steel base material. Following very poor sintering results on these latter materials, they were abandonned. The following results only concern AsMo base materials. Confirmation. was made that green densities were decreased by addition of ceramic phases and solid lubricants. The best results were obtained by compacting at 700 MPa. Densification by dewaxing at 700° C and repressing at 700 MPa increased the sintered density about 4-7%. Finally, granulation was found to improve the compressibility of the powder.

After the first tribological tests, it was decided to suppress any addition of hard particle in the mixes devoted to the future production of valve guides. In that context, the main point was to decide which level of solid lubricants was optimum both in terms of friction properties and of valve guide production. A design of experiment was chosen to determine the amount of MnS (which has been previously shown as the best solid lubricant in terms of compatibility with the matrix) and the best size of these particles. The base material for the design of experiment was as follows :

0.4 % C + 2 % Cu_3P + 97.6 % Astaloy Mo < 75 µm + 0.40 % wax

The MnS content was tested at 5 %, 10 % and 15 'A. MnS sizes were either O -25 µm or 60-120 µm or a 50-50 mixture of these two granulometries. All the mixtures were granulated by HOGANAS. The compressibility of this kind of powders is rather low and the pressure has to be high enough to reach interesting densities, but on the contrary, the tool for the production of valve guide will have very thin walls and core and cannot bear too high pressures. The compaction pressure was then fixed at 700 Mpa. The flow rate is always good, increasing with the % of MnS addition. The size of MnS has no efficient effect, neither on flow rate nor on tap density nor on green density. The green strength is very low (0.2 - 0.3 compared to 2 -2.5 for classical mixes) and affected by the size of MnS particles but not by the % of MnS addition : the bigger the MnS particles, the lower the green strength. On each specimen, superficial longitudinal cracks appeared at the ejection : the spring-back is very high (increasing with the % of MnS addition) and the. green strength very low, which explains, this behaviour. Nevertheless, this could be annoying for the production of valve guide and will have to be taken into account for the design of the tool.

3-b)- Sintering

3-b)-1 - AsMo materials:

Several sintering tests were carried out under different atmospheres on Astaloy Mo based materials. Astaloy Mo combinations without carbon can be sintered under, any atmosphere and temperature except pure H_2 atmosphere (for mixtures with TiC) and Endogas, and sintering time must be 30-45' depending on temperature. For mixtures with carbon sintered at 1120"C, it is better to use synthetic atmospheres like $N_2/5\%H_2/CH_4$ instead of Endogas atmospheres. There is no sintering differences when using Astaloy Mo < 75 pm. The Astaloy PMo combinations with TiC can be sintered only under atmospheres without carbon like $N_2/50\%H_2$ (not pure H_2). The minimum sintering temperature is 1200"C and the sintering time must be 45 minutes. The Mechanical Alloying mixtures must be sintered at low temperature, 1200°C maximum, because the Tii is disolved in the matrix at higher sintering temperature,

Sintering was performed at 1120" C in N_2H_2 atmosphere on the valve guide materials (to be closed to mass production conditions). For these sintering conditions, no consolidation occurs during sintering (no change in density). It is not really important for a part like a valve guide provided that the strength is high enough. The bending strength is very dependent on the % of MnS addition but not on the size of MnS, on the opposite of the green strength !. The level of strength is a little weak for a 15 % addition but seemed to remain acceptable for a valve guide. The hardness is not very affected by the % of MnS and the size of particles except for the highest values (15 % MnS with large granulometry) where a significant drop is observed.

3-b)-2- M 3/2 HSS materials :

In order to avoid batch processes related to vacuum sintering, tests were carried out on HSS using the available conveyor belt and walking beam furnaces under protective atmosphere. These tests were performed by SMK and are to compare to tests made under vacuum.

Composite materials without phosphorus additions (hard phase TiC) showed similar values for the achieved density compared with the materials with phosphorus additions when sintered at 1120”C. Sintering at 1280°C in N_2/H_2 led to a densification of about 90 % cf the theoretical density. Additionally compared to vacuum sintering at 1240”C far better mechanical properties were achieved.

Composite materials without phosphorus additions (hard phase NbC, partially ball milled, various amounts of carbon added) showed a similar behaviour for mesh belt sintering at 1120°C compared to materials with and without phosphorus additions (hard phase TiC) Relative densities of 74% to 78% can thus be achieved. In general mesh belt furnace sintering did not lead to sufficient results. Walking beam furnace sintering at 1280°C revealed very interesting results. Densities near full density were reached, and some density higher than 100 % occured indicating that some reactions e.g. formation of solid solutions took place during sintering.

Composite materials without phosphorus additions (hard phase TiC or NbC; granulated), when sintered in walking beam furnace at 1280°C, revealed almost full density. In some cases, relative density higher than 100% was reached indicating again reactions between NbC and other components at elevated sintering temperatures.

3-b)-3- Vacuum sintering up to 1300°C

Vacuum sintering tests were performed on HSS materials. UoB found that:

M3 class 2 high speed steel + 0.25% C was sintered to full density *in vacuo* at 1240°C. Composite materials based on a powder mixture of M3 class 2 high speed steel + 0.25% C with additions of either monocarbide (5% TiC or 7.74% NbC), singly or with an addition of MnS (5% or 15%) were sintered to full density across the temperature range 1250-1290°C. Sintering characteristics of the composites were determined by a number of factors. The addition of the impure grade of MnS partially decarburised the high speed steel, raising the solidus temperature: The addition of TiC whilst not raising the solidus temperature, did alter the nature and volume fraction of the liquid phase, retarding the rate of sintering, raising the temperature at which full density was attained. NbC had a similar eff ect, but not to such a great extent as TiC; some liquid phase of approximately the same composition as that in the baseline material remained at normal sintering temperatures, the remnants of which were seen as M_6C carbides after sintering. It is possible that the addition of TiC (and NbC to a lesser extent) hindered the rearrangement stage of sintering by acting as sinks for liquid phase before altering the nature of the latter. The principal sintering mechanism (from the sintering kinetics studies) was found to be a type of solution reprecipitation, diffusion controlled solution-reprecipitation. Dissolution of the matrix M_6C carbides together with the added NbC/TiC carbides (when added) into a liquid phase, followed by reprecipitation. to form MC carbides was possibly predominant. Maximum shrinkage exponents of approximately 1/5 were produced in the baseline M3/2, the 5% MnS and the 7.74% NbC composites. Shrinkage exponents produced by the 5% TiC composite were much lower, approximating to 1/10; the presence of TiC, or more precisely, its dissolution into the liquid phase caused this retarding effect on the sintering kinetics of this composite.

Same kind of tests were performed by SMK. Several sintering temperatures close to 1240°C were tested to find out the conditions for highest densification of the materials. The full density of M3/2 has been determined experimentally to 8.08 g/cm^3, i.e. the pure high speed steel powder’ was sintered to 99.5% of the full density at 1234”C. In the case of composite materials containing completely inert phases, the full density can simply be calculated by a linear rule of mixture. While the density of pure M3/2 was very high, the densities of all materials containing TiC and a solid lubricant were relatively low. Therefore the influence of the addition of ferro-phosphorous as sintering aid was studied in a next step. The TiC containing material can be sintered to maximum density at 1210°C while the other compositions sinter even below 1190”C when adding 2% Fe_3P. A further substantial reduction in sintering temperature is reached with 4% Fe_3P.

An overview of the obtained sintered maximum densities for materials 1 B to 15B (according to Table 3) is given, in Table 4. The influence of different amounts of non-metallic additions can be clearly seen. The effect of sintering aids to TiC containing composite materials is very pronounced. In contrast to that, the effect of MA on the densification behaviour was even minor.

Material No.	Full density $[g/cm^3]$		Relative max. density
	calculated	experim.	
1B	8.08	8.04	99.5
2B	7.74	6.85	88.5
3B	7.69	6.86	89.2
4B	7.69	7.63	99.2
5B	7.51	7.42	98.8,
6B	8.03	8.00	99.6
7B	7.70	7.77	100.9
8B	7.64	6.83	89.4
9B	7.64	‘7.59	99.3
10B	7.47	7.38	98.8
11B	7.98	7.98	100.0
12B	7.65	7.78	101.7,
13B	7.60	6.66	87.6
14B	7,60	7.56	99.5
15B	7.43	7.36	99.1

Table 4: Sintered densities for materials 1 B-15B.

As a result of these experiments it was decided to concentrate on composite material systems consisting of a M3/2 matrix with additions of MnS as solid lubricant as well as TiC and/or NbC as hard phases due to the negative effect of alumina. To reduce the number of possible ‘tests to be carried out all partners agreed to work with a "Design-of-Experiments" (DOE). A matrix in which the effect of 4 parameters (ceramic, lubricant, sintering aid and heat treatment) is studied in 8 experiments was chosen. Moreover, 2 reference materials (M3/2 HSS with 2 different heat treatments) were examined. In the first step the appropriate sintering parameters were determined. The effects of the hard phase (TiC or NbC), the amount of the lubricating phase MnS (5 or 15 weight-%), the sintering aid (Cu_3P or Fe_3P) as well as the heat treatment (double temper 550°C or quench 980°C/vacuum & double temper) were studied. The” reference materials did not contain hard phase or lubricating phase and did differ only in heat treatment. The materials 5 through 8 were ball-milled and soft annealed before compaction. After blending the powder mixes were pressed to MPA bars at 600 MPa, lubricant was deburned at 700°C.

Sintering tests were performed at 1150”C, 1220°C, 1243°C, 1273°C and 1285°C in order to determine the appropriate sintering temperature for all samples. It was not always possible to achieve high densities near to full density even at elevated sintering temperatures. But for each configuration, relative densities higher than 90% were reached (see figure 5).

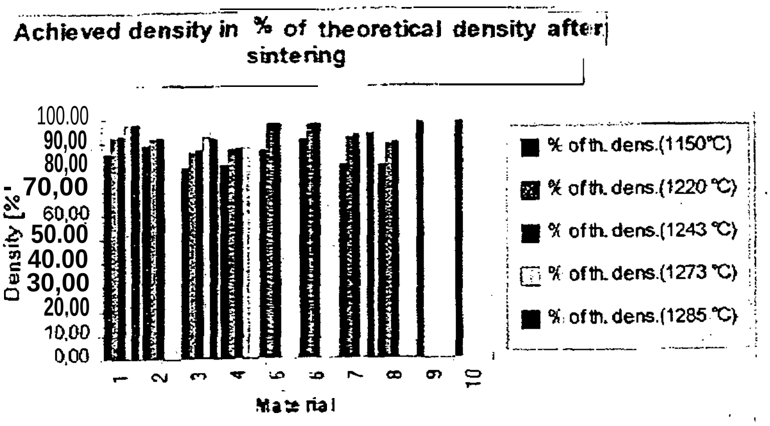


Figure 5: Achieved densities in % of theoretical density after sintering at various temperatures in vacuum. for materials 1 to 10

3-c)- Mechanical properties ‘

In order to obtain first material property data, the SMK M 3/2 HSS materials were hot isostatically pressed after sintering, vacuum hardened from 1160”C and tempered three times at 540°C for 1 hour in air. The hardness was 65 HRC, the microhardness 1150 HV 0.05. The highest TRS values were achieved with pure M3/2. Elimination of the residual porosity by HIPping led to a marked increase of the transverse rupture strength to over 2000 MPa. The material produced from unmilled powder showed thereby slightly higher strength values than the one from milled powder. The densities of composite materials with opened porosity were increased only little by hot isostatic pressing. Furthermore the ‘strength values were hardly affected. While materials containing TiC and CaF_2 besides the M3/2 matrix attained TRS values of 750-900 MPa, the materials containing CaF_2 and MnS showed only values of 200-300 MPa.

Composites studied at UOB have also been subjected to Vickers hardness testing, rupture strength tests and microhardness tests in the as-sintered rendition. In the baseline M3/2 HSS, TRS values of 2200 MPa and hardness of HV 570 were achieved. The inclusion of TiC increased hardness to HV 610 “but a concomitant drop in TRS was noted, to 1810 Mpa. Trials have been conducted to improve the distribution of the fine grade TiC and of the NbC. TRS of 5% NbC containing M3/2 was raised to 2670 MPa when the powders were ball-rolled.

Finally, the AsMo based materials were tested and some basic properties were obtained, specially dimensional change during sintering, density and accuracy. The Astaloy Mo mixtures have higher density when phosphorus is added. The Astaloy PMo mixtures can achieve 95- 97% of relative density when sintering at 1290°C. The use of Astaloy Mo < 75 µm increases density. The TiC and MnS reduce density very much. The MnS mixture of O-25 µm and 60-120 µm powders “(educes the densification level comparing to the conventional MnS. The high sintering temperature produces parts with very bad dimensional accuracy. For Astaloy mixtures, the higher the sintering temperature, the higher the shrinkage. This shrinkage is much higher when phosphorus is added. Finally, the specimens made from Mechanical Alloying powders have the lowest density whatever the sintering temperature be.

Heat treatments have been studied both on M 3/2 HSS materials and on AsMo base materials, for valve seat and valve cap applications.

On HSS matrices, the relatively low hardness values obtained for composite in the as-sintered conditions were improved by post sinter heat treatments : a double temper at 550° C, each for one hour after sintering, was successful in raising the hardness to 750 HV (> 60 HRC) for M3/2 composites. Strength at 1500 MPa was maintained for 5 % TiC addition and dropped to 1100 MPa if 5 % MnS was concurrently added. The salt bath heat treatments used were that of pre-heat, austenitization and step-quench. So far those composites based on M 3/2 HSS and featuring TiC and/or MnS/CaF_2 have been heat-treated using a number of austenization temperatures (1150°C, 1180”C and 1190°C). A complete tempering curve has been produced for samples austenitized at 1180°C, when baseline material hardness peaked at HV 950.

Several heat treatments (carbonitriding, carburizing) were applied on the AsMo based sintered specimens. Heat treatment penetrates until the core specimens due to their low density. Carburized and carbonitrided specimens have almost the same hardness, obtaining about 30-50 HRC depending on the material. After heat treatment, it was necessary to apply a final tempering at 180°C during 60 minutes in order to improve strength and toughness. The most suitable materials for heat treatment were found to be the combinations of Astaloy Mo mixed without carbon and sintered in atmospheres without carbon.

4- EVALUATION OF TRIBOLOGICAL PROPERTIES

Considering the working conditions of the three chosen engine components and the complete expected lack, as the first attempt, of lubricating oil, the “thrust washer” configuration has been considered , as the most appropriate for the friction coefficient ‘measurements. The preliminary screening on the sintered/selflubricant mixtures prepared by Ames, Krebsöge and Sintertech, respectively for Valve cap, Valve seat and Valve guide, was runned with the ”DISC on DISC” test. This method is simple, quick and repeteable and enable rapid screening when many materials mustbe tested and many tests must be done.

Then hot temperature fretting tests have been performed on valve seats materials and some block-on-ring tests were also made by STCH on the AMES valve cap materials.

4-a)- Disc on Disc tests :

The "Disc on Disc" testis a tribosystem made by:
a rotating element (disc made with the sintered material under examination)
a stationary element (disc made of X_{45}CrSiS valve steel)

The test machine is a multisample FALEX FX-1 506 Tribometer, with a test configuration "small thrust washer **T/S". The test machine is completely automatized and computer controlled. The parameter controlled by the system are the load (L) and the rotating speed (V)** between the **contact surfaces. The measured parameters are the temperatures of both the static element and the test environment, the torque (proportional to the Friction Tangential Force operating on the tribosystem) and the Sample Thickness Variation for materials wear.**

The Friction Coefficient (ft.) value is given by the formula:

$$\mu = T/(L \times r)$$

L is the Load applied
T "is the resultant Torque
r is the Average Radius of the contact surfaces.

The first **set of tests was made with** the same **parameter that did not change for all the materials tested (See Table 6).**

Temperature	**"c**	**room**
Load (L)	Lbs	**34**
Specific Load (P)	**MPa**	1
Specimen Area	**mm^2**	**150.72**
Speed (R)	rpm	100
Test Duration	**min**	**1.5**

Table 6: Test conditions

The preliminary screening at room temperature starts with the fc. evaluation on sintered, self lubricant mixture made by the PM companies (table 7):

Table 7: Sintered selflubricating material mixtures tested at room temperature

Firm	**Component**	**Base material**	**Hard phase**	**Solid lub.**	**Sintering ("C)**	**Oil lub.**
AMES	Valve **Cap**	AsMo+2Cu+0.3C	5%TiC	3%MnS	1120	no
		AsMo+2Cu+0.3C	5%TiC	3%MnS	1250	no
		AsMo+2Cu+0.3C	5%TiC	3%MnS	1120	no
		AsMo+2Cu+0.3C (DP)	5%TiC	3%MnS	1120	no
		AsMo+2Cu+0.3C (DP)	5%TiC	3%MnS	1120	yes
		AsMo+2Cu	5%TiC	3%MnS	1120	. no
		AsPMo+2Cu	5%TiC	3%MnS	1250	no
SMK	Valve seat	M3/2				no
		M3/2		5%MnS		no
		M3/2		5%CaF_2		no
		M3/2+5%Fe_3P				no
		M3/2+2%Fe_3P	5%TiC			no
		M3/2+2%Fe_3P		5%MnS		no,
		M3/2+2%Fe_3P		5% CaF_2		no
STCH	**Valve guide**	AsMo+2Cu_3P+0.4C	5%TiC	5%MnS	1120	no
		AsMo+2Cu_3P+0.4C	10%TiC	10%MnS	1120	no
		AsMo+2Cu_3P+0.4C	5%TiC	5%MnS	1200	no
		AsMo+2Cu_3P+0.4C	10%TiC	10%MnS	1200	no

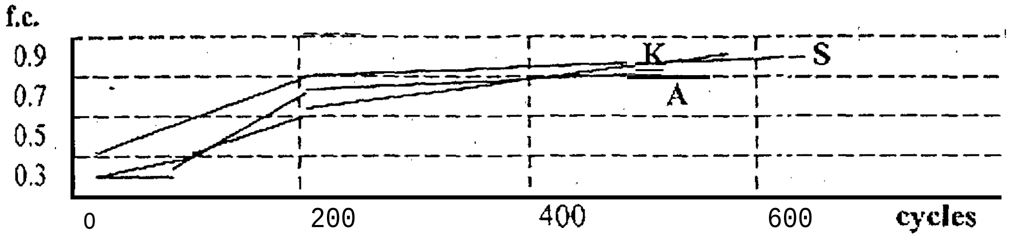


fig. 8 : Average Friction Coefficient (p) measured on the first sintered material mixtures made by Ames(A), Krebsoge(K) and Sintertech(S).

All materials tested shown a fc> 0.5, less than the impregnated samples that produces a fc.= 0.4. Those values were constant for all the tests duration (see fig. 8). Within this context the elimination of the hard phase TiC from the composition of valve cap and valve guide materials was decided. Following the experimental program, new cold friction tests were performed on self lubricating mixtures made by Ames and Sintertech, including oil impregnation on Ames materials and suppression of TiC additions on both. On STCH materials, the new tests showed a decrease of the friction coefficient from 0.8 to 0.6 for higher % of MnS. On the AMES materials (5 to 15% MnS additions in Cold Pmo and AsMo matrices, with and without different oil impregnations), the first tests shown good behaviour for the mixture Cold PMo + 5% MnS not impregnated. The fc. is very near to whom normally shown by a tribosystem with fluid lubricant. On this basis further tests were made on the Cold PMo + 5% MnS sample in comparison with impregnated samples. Increasing the load, the fc. became unstable due to the increasing of interaction between the roughness of the contact surfaces. Anyway the fc. value was acceptable until} 8 Mpa. Increasing the sliding speed, the behaviour of the mentioned sintered mixture became worst. The graph below sintetize the friction behaviour of Cold PMo + 5%MnS.

4-b)- High temperature friction test

Tribological high temperature tests were performed at CSM (Centro Sviluppo Materiali) exclusively on the materials candidate for applications on Valve seat. High temperature friction tests were made with an Optimol SRV machine and settled to generate high frequency alternate sliding motion between a sphere and a stationary disc. The test parameters were chosen as close as possible to the fretting conditions that could be realized between valve and valve seat : .

Disc temperature	“C	600
Frequency	Hz	50
Load	N	100
Oscillation amplitude	mm	2
Duration	min	’15

Two kinds of tests were performed :15 minute test with ‘analysis of friction coefficient and different wear rates and a long term test to check the time to seizing. The sintered self lubricant mixture tested are reported below:

material	composition	Sintering	fc	Ah disc (mm)	Ap sphere (mg)	swa(mm^2)
S14PM	Fe20Cu+40M3/2+1 0Cu+0.7C	1120	0.395	+0.055	-9,6	8.03
G1 UoB	M3/2+ C	1235 Vac	0.377	+0.109	-15.7	9.09
G3	M3/2+7.74NbC+5MnS	1280	0.310	+0.029	-9.4	8.67
G3 UoB	M3t2+7.74NbC+5MnS	1278 Vac	0.327	+0.030	-7.7	7.79
G4	M3/2+7.74NbC+15MnS	1278	0.318	+0.030	-10.0	8.76
1A	M3/2+C	1280	0.312	+0.029 .	-9.0 ’	8.29
1	M3/2+C	1246 Vac	0,302	+ 0.022	-5.3	6.38
G5	M3/2+7.74NbC	1246 Vac	0.303	+0.035	-10.0	9.55
G5 UOB	M3/2+7.74NbC	1246 Vac	0.318	+ 0.074	-7.0	7.80
G6	M3/2+5MnS	1246 Vac	0.308	+ 0.027	-7.7	8.19
G7	M3/2+15MnS	1246 Vac	0.312	+0.028	-8.1	8.24

The materials tested did not show appreciable behaviour differences during the duration. test. Samples G5 UOB and N" 1 seemed to be better than the other materials, particularly with reference to the weight loss and the wear of the sphere. This result was confirmed by long term test : sample N" 1 seized after 49 minutes and sample G5 UOB works more than 60 min. before the seizing occured.

For the final hot engine test at IVECO it was decided to use for the six cylinders one reference material (R) as well as materials G3 and G4 (according to the above table).

4-c)- Block-on-ring test

SINTERTECH developed a bench which can characterize the wear behaviour of materials essentially used in distribution and gear box parts. Characterisation means rapid comparison with reference materials whose behaviour is 'already known. This bench was used to characterize AMES materials for valve cap applications. The principle is well known : friction of a ring (diameter= 40mm, width = 10mm, depth,= 5mm) against a flat (parallelepipedic) sample (5x10x10 mm).

Test conditions :

The tested samples were the same as tested by IVECO in the last Disc-on-Disc test (5 to 15% MnS additions in Cold Pmo and AsMo matrices. with and without different oil impregnations). The surface of the samples has been "polished" with a 1 200 grit paper, in a dry way (no lubricant) to try to obtain the same surface roughness on all the samples.

On the bench, the friction force is registered all along the test, the axial load also. The test conditions are as follows :

- dry friction
- rotating speed of the cylinder= 200 rpm
- test duration = 10 min **(= 2000 cycles)**
- **contact pressure :150 MPa**

Results:

a) Non-impregnated parts :

- Cold PMo alone : μ = 0.19 stable
- Cold PMo + 5 % MnS : μ = 0.19 then increases up to 0.38 and then cold welding occurs.
- Cold PMo + 10% MnS: μ = 0.12 stable
- Cold PMo + 15 % MnS : μ = 0.18 then increases up to 0.35 and then cold welding occurs'.
- Astaloy Mo + 10 % MnS + 2 % Cu + 0.6 % C : μ = **0.15 then increases up to 0.20 and then cold welding occurs.**

b) Impregnated parts

No cold welding occurs for any material using a high temperature synthetic oil. The friction coefficient is 0.11 -0.14 being again the best the Cold PMo + 10% MnS. With a fluorocarbonated oil, the behaviour is the same as without impregnation. The cold welding occurs for all the materials except the Cold PMo + 10 % Mns for which the friction coefficient is 0.21 then increases up to 0.33 and then is stable. Here again these results could be interpreted introducing a competition between the lubrication effect of MnS and the increase of the weakness of the metallic skeleton due to this same MnS. Concerning, the values obtained for friction coefficient, it is difficult (i not impossible) to compare them to those obtained in flat on flat conditions : the contacts are completely different and the applied pressures are not comparable. Anyway, it seems to be possible to obtain good friction coefficient even in dry friction conditions. The addition of oil in the porosity of these materials is beneficial for the high temperature synthetic oil, but disastrous for a fluorocarbonated oil. The problem is now to see the evolution of the oil behaviour in long tests (engine test ?).

5- PROTOTYPE REALIZATION

Some valve seats were produced for the engine test by machining cylinders. The 'valve caps production will be described in parallel with the engine test description. As far as valve guides were concerned, some difficulties appeared when prototyping started. The production of such a cylinder is very difficult by a PM route :

- the ratio "wall depth/length" is very important and it is impossible in that conditions to fill in correctly the die by a classical operation.
- even if the powder is correctly put in the die, the compression operation itself is difficult:
  - the density at the middle of the cylinder could be very low and there is a risk to break it at the ejection.
  - if the density is well distributed, we must find a way to avoid any cracking at the ejection (due to the high spring-back and the low green strength of our materials).

The tool for the valve guide production has been drawn and manufactured. First tests have been conducted by SINTERTECH in order to produce valve guides but some problems appeared rapidly essentially due to a bad control of the compaction parameters. The ejection of the part was really difficult with a very bad surface state and some critical cracks. Nevertheless, the production of such a part seemed still possible. For further tests, modifications were made on the compaction die to increase the ejection's ability. Tests were performed with the 15% MnS mix (lower friction coefficient expected). All the produced guides were broken, either at the ejection or during the manipulation. There are incredibly brittle in the green state ! Furthermore, the density was found homogeneous all along the guides. But after 3 guides produced, the tool has been completely broken. The reasons of such a destruction are still difficult to point out. What is sure is that the lower punch has been broken first, destroying by this way the core rod. The punch has been probably jammed inducing buckling when the table supporting the die went down for ejection. But why the punch has been jammed is not evident. The tool was correctly assembled (i it was not the case, it would have been broken at the first part), the core rod couldn't be stressed in a compressive way. Maybe a bad filling of the die has been responsible for bending of the core rod, inducing jamming. Anyway, the mass production of valves guides with that kind of mixes cannot be imagined. For the engine test, nevertheless, some PM valve guides have been fully machined for examination of their behaviour in real conditions.

6- ENDURANCE ENGINE TEST

6-a)- Electrical engine test :

An IVECO engine was first modified by AMES to make some preliminary tests, mainly on valve cap materials. An electrical engine was used to make the engine work (no fire effect). The first tests were focused on optimizing the working conditions of the engine test and on establishing a test procedure. The first test was carried out under dry conditions and the engine had many problems concerning other parts which were not the valve train. Then, it was decided to work with a certain lubrication, mainly grease lubrication for the rocker arm shaft and only oil vapor lubrication on the distribution parts. A second engine test was then performed to make a first selection. It seems that the best material is' the one based on X-Astaloy Mo, which achieve 50 µm of wear. The Cold PMo based materials experimented higher wear.

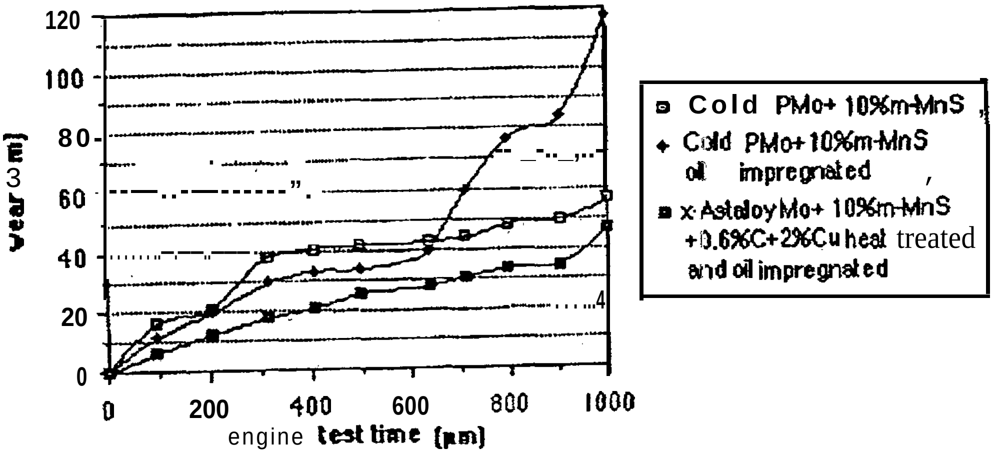


Figure 9: Average results of the second engine test

After looking at these results, several modifications were carried out in order to improve the wear resistance of these materials. Modifications in composition (elimination of copper and reduction of carbon until 0.2% to increase the sizing and sintering densification, addition of some Cold Mo (without phosphorous) to increase hardness and wear resistance and use of normal Astaloy Mo and MnS for reducing costs) and in the valve covers geometry (consisted in modifying its shape in order to make it friendly with PM processes) were achieved. The mixture of Astaloy Mo with copper was also tested as reference to compare the new and old valve cover design. In this way, the manufacturing process for these materials was the following :

- Mixture granulated with 0.4% wax, compacting 600 MPa.
- Sintering 1250°C, 45' in $N_2/5\%H_2/CH_4$.
- Sizing 800 MPa.
- Carburizing 860°C, 30' at 0.88% C + tempering 180°C, 60' and oil protection.

The new materials for the third and fourth electrical engine tests are shown in Table 10.

Test No	Material	Density			Hardness (HRC)
		Real	Theoretical	Relative %	
3	AsMo+10%MnS +0.2%C	PI :6.44 S1 :6.55 P2 :6.85	PI :7.03 S1, P2 :7.25	P2 :94.48	26-31
	x-AsMo+10%m-MnS+0.6%C+2%Cu	P1 :6.34 S1 :6.35 P2 :6.44	P1 :7.02 S1, P2 :7.20	P2 :89.44	21-26
4	x-AsMo+10%m-MnS+0.2%C	P1 :6.00 S1 :6.14 P2 :6.66	P1 :7.03 S1, P2 :7.25	P2 :91.86	26'-31
	x-AsMo+10%m-MnS+10%Cold PMo+0.2%C	PI :6.00 S1 : 6.12 P2 :6.46	P1 :,7.02 S1, P2 :7.24	P2 :89.25	26-29
	Conventional	--------			54-56

Table 10: Tested materials in Test n" 3 and 4.

Regarding test n" 3, the best 'material is the Astaloy Mo+10%MnS+0.2%C. This material had 40 µm of wear after 1,000 hours at the electrical engine. The material x-AstaloyMo + 10%m-MnS + 0.6%C + 2%Cu had higher wear, probably due to its lower density. Test n" 4 shown that the material x-Astaloy Mo + 10%m-MnS + 10%Cold PMo + 0.2%C had 96 µm of wear after 1,000 hours at the electrical engine, higher than the best material of the test n" 3. The material x-AstaloyMo + 10%m-MnS + 0.2%C had the lowest wear, less than the best material of test n" 3 when achieving 1,000 hours. The conventional wrought valve covers had at 1,000 hours the same wear than the best material of test n" 3.

After these results, the material AstaloyMo + 10%MnS + 0.2%C was selected for valve cap for the fired engine test. Prototypes were produced using, a tool, specially designed for this material. The fired engine test was made at IVECO-PEGASO at Barcelona.

6-b)- Endurance engine test :

The valve guides and valve seats were fitted and machined at the fired engine at PEGASO. The test was performed with poor lubrication in order to evaluate differences. The endurance test was carried out with a current production IVECO 8060.45 six cilinders, six liters turbocharged engine.

Material identification

Valve Cap	AsMo + 10% MnS + 0.2% C
Valve Guide	AsMo + 5% MnS +.2% Cu + 0.6% C
Valve Seat	G,3 & G4 (*)

(*) See Table 6.

Material location on ermine and lubrication conditions

CYL. N“	1	2	3	4	5	6
CAP	RM(*)	AsMo + 10% MnS + 0.2% C				RM
GUIDE		AsMo + 5% MnS + 2% Cu + 0.2% C				
SEAT	RM	G3	G3	G 4	G4	G4
‘ CAP LUBRICATION		WITHOUT DIRECT LUBRICATION				

(*) RM. Reference Materials:
CAP: 15NC11 Cmt 1 ‘t, FIAT52123 (Carburized Steel)
SEAT: GhPL7V400 FIAT Cap. 9.02272 (Cast Iron)

Engine test was Carned out according to Standard Method IVECO Engine Endurance Test El. Engine controls during test El were performed regularly. At 480 h, testing was stopped due to an increment in engine blow-by. A valve clearance control led to remove and change exhaust valve caps from cylinders 2, 4 and 5. At 761 h, engine testing was definitively stopped.

Dimensional control on components to be tested was carried out, before and after testing, according to standard practises. Valve seats achieved non acceptable wear. Valve caps behaviour was promising, showing good result on intake cylinder but needing still some improvements on the exhaust application. The valve guide performed very well, both on the intake and exhaust “sides. Furthermore, oil condition was monitored during test El for engine control: Oil analyses results shown that all parameters were below critical values for this engine. However, Mo contents indicated significative sintered material wearing. Oil Consumption Test was carried out according to IVECO Testing Method F47. Average Oil Consumption during test. was 0.32 gr/CVh. Average Reference Oil Consumption Value for this engine is 0.40 ± 0.05 gr/CVh. A significant decrease in oil consumption of nearly 20% has then be achieved using these materials.