TRIBOLOGICAL EFFECT OF NITRO- AND NITRO-CARBURIZING TREATMENTS ON Mo-Fe SINTERED ALLOYS EVALUATED BY DOE (DESIGN OF EXPERIMENT)

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SUMMARY
Two Fe-1.5Mo sintered alloys produced from pre-alloyed powders were studied. After sintering, surface properties were modified by nitro- and nitrocarburizing thermochemical treatments. Materials properties were investigated by optical and scanning electron microscopy, surface hardness tests, and microhardness profiles. Chemical and phases variations were studied by EDS analysis and X ray diffraction. Dry sliding tribological tests were carried out using a flat on cylinder geometry. A DOE with $2^2$ factorial experiment was set out, varying between 2 levels the input factors: (1) carbon percentage in the sintered alloy and (2) propane percentage in the atmosphere of the thermochemical treatment. The mathematical model of system response was developed describing the influence of both input factors and their interaction on the maximum wear scar depth (the selected output).

Keywords: tribology, sintering, nitrocarburizing, DOE, ANOVA

1 INTRODUCTION
In the last years many methods for planning experimental campaigns were developed. Among those, DOE (Design Of Experiment) is an experimental strategy particularly powerful: it aims at obtaining the maximum amount of information about a system from a limited number of tests, investigating the individual effect of each factor (main effect) and determining at the same time whether the factors interact [1-3]. The experimental information is organized in a mathematical model describing the system response as a function of the controlled variables, in order to find the most robust system, invariant to the variation of uncontrolled variables. Furthermore DOE allows to estimates experimental conditions in which the system response assumes a predetermined value (with an established probability).

In the present work, DOE was applied to analyse a tribological problem: the wear resistance of surface hardened sintered alloys.

2 EXPERIMENTAL
2.1 Materials
Two Fe-1.5Mo sintered alloys were obtained from pre-alloyed powders: the percentage of C was $<0.01\%$ in A01 [4,5] and about 0.5% in A5 [6]. Sintering process steps and final values of physical and mechanical properties of alloys are summarised in table I. During A01 pre-sintering and sintering steps the atmosphere was 90% N$_2$ and 10% H$_2$; during A5 sintering the atmosphere was endogas (20% CO, 40% H$_2$, 40% N$_2$).

<table>
<thead>
<tr>
<th>A01</th>
<th>Sintering process:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ø Cold pressing (P=590MPa)</td>
<td></td>
</tr>
<tr>
<td>Ø Pre-sintering (20 min. at 850°C)</td>
<td></td>
</tr>
<tr>
<td>Compacting (P=785MPa)</td>
<td></td>
</tr>
<tr>
<td>Ø Sintering (30 min at 1120°C)</td>
<td></td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>7.55</td>
</tr>
<tr>
<td>Hardness HV$_1$</td>
<td>115</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A5</th>
<th>Sintering process:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ø Compacting (P=400MPa)</td>
<td></td>
</tr>
<tr>
<td>Ø Sintering (30 min at 1120°C)</td>
<td></td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>6.47</td>
</tr>
<tr>
<td>Hardness HV$_1$</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 1: Sintering conditions and physical properties of the alloys A01 and A.

Figure 1: OM micrograph of A01 alloy
The OM/SEM microstructures of the sintered alloys are shown in figures 1 and 2: A01 is ferritic with some bainitic islands, while A5 is completely bainitic.

### 2.2 Thermochemical treatments

To obtain hardened surface layers, two different thermochemical treatments (TCT) were carried out on both A01 and A5 alloys: (i) N (nitriding) and (ii) NC (nitrocarburising). Samples were treated for 8 h at 590°C and 4 mbar. The thermochemical treatments differed for the % composition of the atmosphere:

- **N**: 25 H₂ 75 N₂
- **NC**: 20 H₂ 75 N₂ 5 propane

Post-treatment properties of sintered alloys are summarized in table II.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface hardness HV₀.₀₅ (µm)</th>
<th>TCT depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A01 N</td>
<td>410</td>
<td>200</td>
</tr>
<tr>
<td>A01 NC</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>A5 N</td>
<td>350</td>
<td>600</td>
</tr>
<tr>
<td>A5 NC</td>
<td>650</td>
<td>650</td>
</tr>
</tbody>
</table>

*Table 2: Vickers hardness and depth of the surface hardened layer of sintered alloy*

X Ray Diffraction analysis on N-treated sintered alloys, revealed the presence of Fe₄N in the hardened layer. The main product of NC treatment is Fe₃(C,N) with a like-Fe₃C (cementite) lattice. Some optical micrographs of hardened layer of alloys are shown in figures 3 and 4.

### 2.3 DOE application

The Design Of the present Experiment was organised in the following steps:

- **FSE (Factors Screening Experiment):** it is the selection of input variables which reasonably have the main influences on the output parameter i.e. the system response;
- **DOE (Design Of Experiment):** i.e. the design of experimental tests in order to individuate the conditions in which the system is invariant (robust). After the execution of experimental tests it is possible to develop a mathematical model that estimates the output parameter.
- **ANOVA (ANalysis Of VAriance):** it is the investigation of factors affecting the variance of data, in order to estimate the influence of the random error.

#### 2.3.1 FSE

In a preliminary step of the experiment, the two input factors (varying between two levels) were identified with: x₁ the C percentage in the alloy (<0.01 % in A01 and 0.5 % in A5); x₂ the propane content in the TCT atmosphere (0 % in N and 5 % in NC). The selected output parameter y was the depth of the wear track at the end of tribological tests [7].

#### 2.3.2 DOE

Unidirectional dry sliding tests were carried out using a slider-on-cylinder geometry in laboratory air and room temperature [2]. The test conditions were:

- applied load: 10 N;
- sliding speed: 0.3 m/s;
- sliding distance: 10000 m.

The stationary slider was the TCT sintered alloy while the counter-facing material was a quenched and tempered C55 steel cylinder (52 HRC). Friction force and total wear (slider + cylinder) were continuously recorded as a function of sliding distance. The depth of the wear tracks was measured by stylus profilometry at the end of the tests.

An useful tool of DOE is the design matrix (table III) which allows to organize experimental tests. x₁ and x₂
are the parameterised input variables, indicating +1 and –1 the higher and the lower values respectively. The interaction effect between the input variables is valuable from the column $x_1 \cdot x_2$ (built with the results of the product of the previous two columns $x_1$ and $x_2$). The results of tribological tests (mean value of two replications) are presented in the last column of table III. The total number $T$ of experimental tests to carry out is computed by equation (1):

$$T=n \cdot (L)^V$$  \hspace{1cm} (1)

where:

- $n =$ number of replication of the same experiment (=2)
- $L =$ number of levels (=2)
- $V =$ number of the input variables (=2)

<table>
<thead>
<tr>
<th>Test</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_1 \cdot x_2$</th>
<th>$y$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1 (A01)</td>
<td>-1 (N)</td>
<td>+1</td>
<td>18.3</td>
</tr>
<tr>
<td>2</td>
<td>-1 (A01)</td>
<td>+1 (NC)</td>
<td>-1</td>
<td>81.1</td>
</tr>
<tr>
<td>3</td>
<td>+1 (A5)</td>
<td>-1 (N)</td>
<td>-1</td>
<td>6.7</td>
</tr>
<tr>
<td>4</td>
<td>+1 (A5)</td>
<td>+1 (NC)</td>
<td>+1</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Table 3: DOE design matrix for organisation of the experimental tests and results.

On the basis of table III it is possible to compare the wear resistance of samples. The best performances (minimum wear) are shown by:

- the alloy A5
- the N thermochemical treatment.

The combination of A5 and N provides the most wear resistant samples (6.7 $\mu$m of wear scar depth).

The result $y = 81.1 \mu$m, obtained combining NC TCT and A01 alloy is about 1 order of magnitude higher than the results of the other tests. This underline the importance of taking in the opportune consideration the effect of synergic interactions among input variables on the system response.

The design matrix (table III) allows the development the following mathematical model:

$$y = 28.6 - 21.1 x_1 + 16.1 x_2 - 15.3 x_1 x_2$$  \hspace{1cm} (2)

describing the dependence of sample wear from the presence of carbon ($x_1$) in the alloy and the presence of propane in the thermochemical atmosphere ($x_2$). The statistical significance of numerical coefficients in equation (2) (analyzed by the T-Student test) was 95%.

From the mathematical model (2) it is possible to derive the following considerations:

- both the selected input variables and their interaction have an influence on the system response.
- Even if $x_1$ appears to cause the higher effect on $y$, the numerical coefficients in the equation (2) are indicatively of the same order of magnitude; consequently all the input factors (main and of interaction) have a comparable weight in influencing wear.

Some further considerations can be made simplifying the model in particular cases. The plot (figure 5) of wear vs. propane percentage in the thermochemical atmosphere in the form of the parameterized variable $x_2$, is built solving equation (2) for $x_1 = -1$ and $x_2 = +1$ (A01 and A5 alloys respectively).

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The low slope (0.8) of the line corresponding to the TCT A5 alloy compared with the slope (31.4) of the TCT A01 line is an index of the low influence of the kind of TCT on A5 wear resistance: the system constituted by A5 alloy is more robust than the A01 one.

In the same way the plot (figure 6) of wear vs. carbon percentage in the sintered alloys in the form of the parameterized variable $x_1$, is built solving the equation (2) for $x_2 = \pm 1$ (NC and N thermochemical treatments).

In figure 6 the slope of the N line (-5.8) is lower than the slope (-36.4) of the NC line. In other terms, the effect of N TCT on sintered alloys is more constant than the effect of NC thermochemical treatment: the thermochemical treatment N is more robust than NC.

It is also important to complete this section analysing some approximations made in designing the present experiment. The input variables selected in the FSE step couldn’t be the only ones influencing the response. In particular the sintering conditions (pressure, temperature and exposure time in the sintering process) are probably quite important to determine the wear resistance of sintered materials.
2.3.3 ANOVA

ANOVA (ANalysis Of VAriance) was used in order to analyse the role of the random error in influencing the results of tribological tests. The total variance of data $S_{\text{S}_{\text{total}}}$ is decomposed in different causes of variance, calculated by equation (3) [1]:

$$S_{\text{S}_{\text{total}}} = S_{\text{S}_{\text{overall mean}}} + S_{\text{S}_{\text{among tests}}} + S_{\text{S}_{\text{between replications}}}$$  (3)

Results are presented in graphic form in figure 7. It can be noticed the low influence (1.8%) of random error ($S_{\text{S}_{\text{between replications}}}$) on the total Sum of Squares ($S_{\text{S}_{\text{total}}}$).

![ANOVA diagram]

Figure 7: distribution of the different source of variance

3 CONCLUSIONS

Experimental tests on Fe-1.5 Mo sintered alloys (i) with or without carbon; (ii) thermochemically treated by nitriding or by nitrocarburising, were carried out. The wear resistance was higher for the alloy containing high percentage of carbon, and for the TCT atmosphere without propane (nitriding). The combination of nitriding thermochemical treatment and high carbon alloys presented the best wear behaviour.

DOE analysis showed that the most robust system (less invariant to the variation of uncontrolled variables) is constituted by the high carbon sintered alloy: its wear resistance is indicatively constant with the variation of propane content in the thermochemical atmosphere.

4 REFERENCES