EFFECT OF PROCESSING CONDITIONS ON THE WEAR BEHAVIOUR OF PREALLOYED SINTERED STEELS Fe (Cr -Mo) WITH ADDITION OF Cu AND C

M. Actis Grande, R. Bidulský, J. Bidulská and I. Forno

Abstract

The main aim of the present paper is to show the influence of high temperature sintering and of cooling rates on the wear behaviour of prealloyed sintered steel Fe (Cr -Mo) with addition of Cu and C. The wear behaviour of the sintered steels was investigated through pin-on-disk tests. Two different processing conditions have been used, involving different cooling rates from the sintering temperatures (1180 and 1240°C), the first of which, identified as slow, implied a cooling rate of 0.05°C/s. The other cooling rate determined an average cooling of 6°C/s (rapid cooling). The microstructures of sintered specimens obtained through slow cooling conditions were heterogeneous and complex. The aim of investigation was to identify the effect of sintering temperature and cooling rate on shifting a portion of pearlite-bainite to favourably portion of martensite-bainite with effective improvement of the wear characteristics (including wear rate, wear resistance and friction coefficient) of Fe-Cr-Mo-[Cu] sintered steels. The role of the different chemical compositions has also been evaluated.

Keywords: prealloyed sintered steels, sliding wear, sinter hardening, microstructure

INTRODUCTION

In the present time, in powder metallurgy (PM) are generally used are different alloying elements such as, nickel, molybdenum, manganese and chromium. This latter, in particular, is currently quite diffused since it increases the hardenability of the steels, provides superior strength and it is basically cheap. In addition, by prealloying, better dimensional stability during sintering can be achieved in comparison to diffusion alloying. Prealloyed materials have become more and more used in the PM industry. One reason for this is that the core of the iron particle is strengthened and as a consequence the mechanical properties are enhanced [1-6].

During sintering of chromium prealloyed alloys it is important to avoid oxidation during powder fabrication, as well as during subsequent processing stages; in particular a suitable sintering atmosphere with adequate dew point [2-9] is required to guarantee good final products.

One modern method that allows integrated rapid cooling sufficient to transform a significant portion of the matrix microstructure to martensite, which results in a significant increase of mechanical properties, including of wear resistance of the sintered alloys, is sinter hardening [7-9]. Moreover, by prealloying the iron powder, the activity of chromium decreases and prealloyed materials are well suited for sinter hardening. Vacuum furnace
allows the possibility of programming in order to perform quenching and tempering treatments integrated in the same cycle, thus reducing internal stresses that cause excessive notch sensitivity and brittleness.

This work is focused on the role of the sintering temperatures and on the effect of the different cooling rates on the wear resistance of Fe (Cr-Mo) - [0-2% Cu] - 0.65% C sintered steels. Mass losses were expressed as material removal during the test and were recorded as function of the sliding distance. The wear of sintered materials is more complicated than that of wrought steels and depends on some factors related to the sintered microstructures, such as plasticity and strength of the different phases, as well as porosity [8]. Hence, the evaluation of the wear resistance (as the reciprocal value of the amount of wear) is better expressed in terms of wear rate. The wear rate has been calculated using the following equation:

\[ W_s = \frac{\Delta m}{\rho \cdot L \cdot F_N} \]  

(1)

where: \( W_s \) is the wear rate \([\text{cm}^3/\text{Nm}]\), \( \Delta m \) is the mass loss of test samples during wear test \([\text{g}]\), \( \rho \) is the density of test materials \([\text{g/cm}^3]\), \( L \) is total sliding distance \([\text{m}]\), \( F_N \) is the normal force on the pin \([\text{N}]\).

**MATERIAL AND EXPERIMENTAL METHODS**

The starting powders were: Astaloy CrL powder (Höganäs AB), commercial electrolytic Cu (particle size less than 40 µm), graphite powder and commercial AW wax powder as lubricant. The final mixtures were homogenised in a Turbula mixer. Formulations are reported in Table 1.

Tab.1. Characterization of the studied composition.

<table>
<thead>
<tr>
<th>Alloy No</th>
<th>Composition (in wt. %)</th>
<th>Type of used powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fe-1.5Cr-0.2Mo-0.65C</td>
<td>Astaloy CrL, graphite</td>
</tr>
<tr>
<td>B</td>
<td>Fe-1.5Cr-0.2 Mo-1Cu-0.65C</td>
<td>Astaloy CrL, electrolytic Cu, graphite</td>
</tr>
<tr>
<td>C</td>
<td>Fe-1.5Cr-0.2 Mo-2Cu-0.65C</td>
<td>Astaloy CrL, electrolytic Cu, graphite</td>
</tr>
</tbody>
</table>

Specimens were obtained using a 2000 kN hydraulic press, in a disc-shaped mould (φ 40 mm) applying a pressure of 600 MPa. Sintering was carried out in a TAV vacuum furnace with argon back filling at 1180°C and 1240°C for 3600 s. The slow cooling condition was 0.05 °C/s while the rapid cooling condition (sinter hardening) of 6°C/s. Densities were evaluated using the water displacement method.

Pin-on-disc wear test was carried out by means of a tribometer entirely developed in the Alessandria Campus of Politecnico di Torino. The disc was made of the investigated material. As a counter face, a WC-Co pin was used, having a rounded shape on top with φ 3 mm. The counter-pin was changed after the end of each test, in order to preserve the roundness of its top. All wear tests were performed in air and without any lubricant. The applied loads were 25 N. The rotation speed of the disc was 140 rpm. The tested surface was polished with abrasive papers in order to determine a medium surface roughness equal (or less) to 0.8 µm, as specified in the ASTM G99–95a. Each test was interrupted after 300, 600, 900, 1200 and 2000 meters sliding distance and discs were weighed.
Microstructures features observations were carried out using light and SE microscopy (LEICA and JEOL 7000F). The apparent Rockwell hardness HRA (measured on the tested specimen surfaces) was determined by means of digital tester EMCOTEST and microhardness, HV 0.1, according to the standards ASTM E 18 for Rockwell hardness and ASTM E92 for Vickers hardness.

**EXPERIMENTAL RESULTS AND DISCUSSION**

Table 2 reports the density values before and after sintering as well as the relative values.

<table>
<thead>
<tr>
<th>No.</th>
<th>P*</th>
<th>S*</th>
<th>ΔV/V</th>
<th>H</th>
<th>P*</th>
<th>S*</th>
<th>ΔV/V</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.98</td>
<td>7.00</td>
<td>-1.11</td>
<td>46.45</td>
<td>6.98</td>
<td>6.97</td>
<td>-0.65</td>
<td>63.70</td>
</tr>
<tr>
<td>B</td>
<td>6.98</td>
<td>6.97</td>
<td>-0.71</td>
<td>49.05</td>
<td>6.97</td>
<td>6.96</td>
<td>-0.53</td>
<td>70.80</td>
</tr>
<tr>
<td>C</td>
<td>6.98</td>
<td>6.97</td>
<td>-0.87</td>
<td>51.80</td>
<td>6.98</td>
<td>6.96</td>
<td>-0.49</td>
<td>70.68</td>
</tr>
</tbody>
</table>

*SC-slow cooling rate, RC-rapid cooling rate,*P-green density, *S-sintered density, *H-Hardness

A small decrease in the as-sintered density, compared to the green density, was recorded. The volume changes (ΔV/V), in relation to the Cu addition, were in the range of -0.49% to -2.2%, with negligible differences in relation to the C and Cu contents. The relatively largest decrease of the volume (ΔV/V) of -1.33% to -2.2% was recorded in the samples rapidly cooled from the higher temperature (1240°C). It is well-known that copper increases the dimensions of parts after sintering, on the contrary the undesirable growth that occurs is decreased when graphite is used in combination [7].

The microstructures of investigated sintered alloys are complex and heterogeneous. Microstructure investigations as well as fracture surface observation were communicated in a previous article [7] for sintering at 1180°C. Microstructure plays an important role in the wear behaviour in PM materials, therefore the microstructure is summarised as follows: Specimens A in slow cooled conditions showed dominant pearlite microstructure with small ferrite areas. The application of rapid cooling to the same system resulted in dominant bainitic microstructures with some martensite. In the system B, the addition of 1% Cu formed a mixture of fine pearlite and some bainite. Rapid cooling condition led to the formation of a mix of bainite and martensite. The microstructure of system C, where a 2% of Cu was added consists of a mixture of fine pearlite and some bainite. As for the system B, the rapid cooling condition led, also in this case, to the formation of a mix of bainite and martensite. The evaluation of the results deriving from the rapid cooling from the sintering temperature of 1180°C showed that increasing the Cu content resulted in an increase of amount of bainite/martensite. The microhardness values put into evidence that the value is ranging from (138-240 HV 0.1) to (313-648 HV 0.1) in the system A, from (137-296 HV 0.1) to (313-648 H V0.1) in the system B, from (146-303 HV 0.1) to (485-701 HV 0.1) in the system C. Increasing the sintering temperature to 1240°C resulted in the formation of a dominant martensitic microstructure. The following figures, Figs.1 a-c, report the microstructures of the 1240°C sintered materials.
The sintering temperature promotes the formation of a liquid phase (based on Cu) and then activates the sintering process [7, 10-15]. In the system A (without Cu content), the apparent hardness shows lower values in comparison with systems B and C. The higher hardness values for both systems with Cu content (B and C) are similar, but system B has a more homogeneous distribution of martensite in the matrix. Copper increases hardenability, and favours the formation of martensite in the Cu-rich areas, which also contributes to hardening. A substitutional solid solution occurs in Fe-Cu because: Fe and Cu both crystallize in the face-centered cubic structure, have similar atomic radii, electronegativities, and valences according to Hume Rothery rules [16].

Coming to the wear test results, Figs.2a, b show the wear rates obtained according to equation (1).
Fig. 2a. Wear rates of the specimens sintered at temperature of 1180°C and followed by slow cooled rate and rapid cooling rate.

Fig. 2b. Wear rates of the specimens sintered at temperature of 1240°C and followed by slow cooled rate and rapid cooling rate.

For the specimens sintered and slow cooled the highest wear rate values were recorded. The high sintering temperature at 1240°C \( (W_s \approx 30 \times 10^{-11} \, \text{cm}^3/\text{Nm}) \) results in a wear rate two orders of magnitude better in comparison with sintering temperature of 1180°C \( (W_s \approx 100 \times 10^{-13} \, \text{cm}^3/\text{Nm}) \). In terms of microstructure, raising the sintering temperature from 1180°C to 1240°C is beneficial for the wear resistance of studied materials, due to the formation of more developed sintering necks between the powder particles. Wear rates of sintered Fe (Cr-Mo) - [0-2% Cu] – 0.65% C steels using higher temperature and cooling rate (sinter hardening) also were improved due to the shifting of ferrite - bainite to dominant martensitic microstructure with some areas of bainite. The wear rates can be related to chemical composition, volume of different microstructural constituents, as well as the matrix hardness.

Table 3 reports the steady-state value of friction coefficient and shows how the porosity content influences the steady-state value of friction coefficient.

<table>
<thead>
<tr>
<th>No</th>
<th>1180°C / SC / density</th>
<th>1180°C / RC / density</th>
<th>1240°C / RC / density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P_Total [%]</td>
<td>( \mu_{ss} ) [-]</td>
<td>P_Total [%]</td>
</tr>
<tr>
<td>A</td>
<td>8.64</td>
<td>0.7000</td>
<td>9.01</td>
</tr>
<tr>
<td>B</td>
<td>9.73</td>
<td>0.6870</td>
<td>9.91</td>
</tr>
<tr>
<td>C</td>
<td>9.82</td>
<td>0.5994</td>
<td>9.98</td>
</tr>
</tbody>
</table>

The results show that the steady-state value of friction coefficient decreases with the increasing amount of porosity. Using traditional PM methods, cold die pressing and following sintering operations, porosity value of 8-10% are usually obtained, depending on the sintered steel characteristics such as alloying additions and microstructural constituents. The friction properties are strongly dependent on the sintered steel characteristics.

Figure 3 shows the trend of the friction coefficient as function of the sliding distance for the system A.
Fig.3. The curve of the friction coefficient of the system A sintered at 1180°C and slowly cooled.

It is seen that the friction coefficient at the beginning of the test steeply rises to about 0.9 between the distance of 100 and 150 m. Further sliding shows reduction of the friction coefficient which reaches a steady state. The steady state stage was observed after approximately 800 m of sliding.

Useful information on the wear mechanisms of the sintered steels was obtained by SEM analyses of the worn surfaces. The worn surfaces were characterized by the presence of fine grooves parallel to the sliding direction and flake-like fragments, typical of delamination wear, observed in the wear debris (Figs.4 and 5).

Fig.4a. The worn surfaces of the specimens A sintered at temperature of 1180°C and slowly cooled.

Fig.4b. The worn surfaces of the specimens B sintered at temperature of 1180°C and slowly cooled.
Fig. 4c. The worn surfaces of the specimens C sintered at temperature of 1180°C and slowly cooled.

Fig. 5a. The worn surfaces of the specimens A sintered at temperature of 1240°C and rapidly cooled.

Fig. 5b. The worn surfaces of the specimens B sintered at temperature of 1240°C and rapidly cooled.

Fig. 5c. The worn surfaces of the specimens C sintered at temperature of 1240°C and rapidly cooled.

The delamination wear mechanism postulates consecutive steps of gross plastic deformation of the subsurface along the sliding direction, the subsequent nucleation of voids and cracks. Remembering the fact that in PM materials, the voids preexist in the form
of pores; pores act as stress and strain concentrators, then the nucleation of cracks might be favoured. The propagation of the cracks occurred nearly parallel to the wear surface and so the formation of wear sheets when cracks reached the surface. Therefore, plastic deformation took place on wear surfaces during wear tests. The surface of chromium pre-alloyed powder is covered by a surface oxide layer consisting of mainly complex refractory oxides, inhomogeneous in thickness (Figs.6a-6c). Detailed description of amount and type of oxides present is reported in [9].

Karlsson et al. [2, 17] revealed that the above mentioned surface oxides are formed by a continuous iron oxide layer with a thickness of approximately 5.5-7 nm with the presence of some particulate compounds characterized by a high content of strong oxide forming elements such as Cr, Mn and Si. In contrast to internal oxides (according to Ortiz [19] are spherical and are Cr and O rich of the type $M_2O_3$ with 100-500 nm in dimension) they do not have any significant influence on the final mechanical properties of the sintered component. The surface oxides are barriers for diffusion and will retard proper neck formation during sintering [20-23]. Hryha et al. [24] observed, within the dimples of interparticle ductile fracture, facets with mainly complex refractory oxides with a dominant content of chromium oxide. This inhibits extensive intermetallic contact and adhesion
between the sliding counterfaces of the wear system and leads to preferential shearing within the oxide. Another source of oxide during sliding, according to Scott [25], is oxidation of metallic debris. Thus, such wear debris particles, produced in the early stages, may be broken up and reduced in size by the sliding action, thereby exposing fresh areas of clean metal for further oxidation. The extent of such oxidation can be considerable, since the rate of initial or transient oxidation can be relatively rapid, while the surface area of exposed metal may be large. During sliding, the oxidation process is promoted by the heat of deformation and the increased energy of the particles due to the increased defect density and surface energy. Also, if the heat of oxidation released is taken into account, fine metallic particles may be oxidized spontaneously and completely under some conditions. Hence, a considerable amount of oxide can be generated during low-speed sliding [26], even at low temperatures. The resulting oxide debris can develop into a wear-protective layer.

The interpretation of the role of porosity on the wear resistance is not as simple as for the mechanical properties. The pores are filled with debris particles during wear if the amount of porosity is higher than 8-10% and the pore size is bigger than 10 µm [9, 19, 23]. This enhances the wear resistance of the samples by increasing the real contact area and decreasing the contact pressure. The small wear debris can be trapped inside the open pores on the sliding surface, and this may lead to the main difference between the wear rate obtained from the depth loss and from the weight loss. However, the higher sintering temperature enhances roundness and an overall reduction of pores, therefore promoting a significant increase of wear resistance. Nevertheless, porosity can be beneficial by enhancing the wear resistance by entrapping the wear debris and preventing the formation of large abrasive agglomerates.

The mass loss decreased with the increase in the hardness level. It is very clear that investigated steels, with less hard microstructures, wear more than the harder microstructures. As the hardness of the microstructures of investigated steels increases, the wear resistance also increases. By reason of processing condition regulation, the relation between the hardness (measured on the tested specimen’s surfaces) and the values of mass loss (Fig.7a,b) shows the effect of both surface hardness and microstructure on the wear behaviour of the tested alloys.

![Fig.7a](image_url)  The results of both surface hardness and microstructure on the wear behaviour of the studied alloys.

![Fig.7b](image_url)  The exponential dependence of both surface hardness and microstructure on the wear behaviour of the studied alloys.
Hence, microstructures have a dominant influence on the behaviour of the surface (and sub-surface) areas, in connection to porosity, especially when no surface densification (through shot peening or surface rolling) is applied.

**CONCLUSION**

Wear resistance of investigate sintered steels using higher temperature and cooling rate (sinter hardening) were improved due to shifting of ferrite - bainite to dominant martensitic microstructure. The prevailing wear mechanism of the sintered steels is the delamination wear mechanism. The worn surfaces were characterized by the presence of fine grooves parallel to the sliding direction and flake-like fragments. The proposed exponential relation between the hardness and the values of mass loss shows the effect of both surface hardness and microstructure on the wear behaviour of the tested alloys. Therefore, the microstructure characteristics represent an important parameter affecting the wear behaviour of studied sintered steels, especially when no surface densification is applied.

**Acknowledgements**

R. Bidulský thanks the Politecnico di Torino, the Regione Piemonte, and the CRT Foundation for co-funding the fellowship.

**REFERENCES**