THE INFLUENCE OF FIRST COMPACTION ON PROPERTIES AND MICROSTRUCTURE OF DOUBLE PRESSED Cr-Mo PREALLOYED SINTERED STEEL

M. Azadbeh, H. Danninger, Ch. Gierl-Mayer

Abstract

Double compaction is an attractive method for attaining higher density in powder metallurgy parts; this holds also for new material systems such as Cr-Mo alloyed steels. The chances of improving density in the repressing step depend on many factors such as type of material, first and second compacting pressures, intermediate annealing temperature and time. The principal aim of this research was to show the role of the first compacting pressure in obtaining higher densities and thus better mechanical properties for 1.5%Cr-0.2%Mo prealloyed steel. It could be observed that the density of samples repressed at a given second pressure increases with higher first compacting pressure. Higher stress and deformation in the more work hardened specimens are helpful with regard to enhancing carbon dissolution as well as softening of the matrix during the intermediate annealing step. On the other hand, differences in the extent of powder particle contacts as a consequence of varying first compacting pressures, as well as the number of necks generated between particles – which provide diffusion paths - and their volume growth during the intermediate annealing process are responsible for the repressed - and in consequence the sintered - properties of samples. Also the “inverse” core-rim microstructure generated during annealing of compacts from these Cr-Mo prealloyed grades is beneficial for densification during repressing.

Key words: sintered steel, double pressing, Cr-Mo alloy steels, compacting pressure

INTRODUCTION

The increasing use of powder metallurgy components for applications that require improved mechanical properties generates a need to understand the factors controlling these characteristics.

Several methods are under development to increase the load bearing capacity of sintered ferrous materials. The major trends of these methods are the alloy development and/or modification of the manufacturing process [1, 2]. In contrast to the processing of ceramics or hardmetals, marked densification during sintering is usually not desirable for PM precision parts to avoid loss of geometrical precision (although MIM has shown that it can be done successfully). Therefore, the density required for attaining the mechanical properties has to be established during compaction. On the other hand, at least in industrial practice cold compacting of ferrous materials is limited to density levels of about 7.1 g.cm$^{-3}$

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maximum due to work hardening processes. For attaining higher densities, either warm compaction [3] or high velocity compaction [4] can be carried out, or double pressing can be employed.

Double compacting – also referred to as double-press-double-sintering process, DPDS, is one of the beneficial techniques which increase the density of PM materials and, as a result, enhance the mechanical properties [5-7]. (In most cases it is not really a “double sintering” since the first heat treatment is done at fairly low temperatures, as will be described below). The increase in density depends on many factors such as first and second compacting pressures as well as annealing temperature and time, which are strongly related to have a pronounced effect on removing the work hardening introduced in the first compacting step. A further limiting factor is the volume of the compact taken by the added carbon – usually admixed graphite –, since this volume is incompressible during compaction but is turned to void during sintering, as a consequence of carbon dissolution in the ferrous matrix. Thus any volume filled by graphite during the (second) pressing generates porosity during subsequent sintering that must be regarded as inevitable.

In compaction processes, strain hardening effects and work hardening of grains during the compression must be taken into account [8]. Therefore it can be concluded that work hardening occurs during compaction [9]. In repressing, the compacted samples are then to be further densified by a second pressing step; therefore they need intermediate annealing to eliminate or at least alleviate work hardening [10]. When a cold worked metal is heated, softening occurs through recovery and recrystallization. Cold working usually decreases the ductility of the metal but increases the strength, and during annealing/recovery these properties return gradually to their original values and internal stresses decrease [11].

Generally, work hardening is more completely removed at higher annealing temperatures [12], but in [13, 14] it has been shown that for carbon-containing steel compacts, a “window” for the annealing temperature can be defined within which the amount of carbon – usually admixed graphite – dissolved is still too small to exert a significantly adverse effect on the compressibility, while being sufficiently high to generate empty space that can be compressed during repressing.

MATERIALS AND METHODS

Prealloyed steel powder Fe-1.5%Cr-0.2%Mo (Astaloy CrL, Höganäs AB) was mixed with 0.6% C (natural graphite UF4), and the mix was uniaxially compacted at different pressures, 200 – 400 – 600 MPa, to bars with rectangular shape (impact bars ISO 5754, 55 × 10 × approx. 8.5 mm) in a pressing tool with floating die. Die wall lubrication was afforded by MULTICAL sizing oil. The green density was calculated by measuring the compact mass and dimensions. Then the samples were put into an open boat made of mild steel and annealed in a small laboratory tube furnace for 30 min at 850°C in flowing N₂ of 99.999% purity with subsequent cooling from 850°C to 601°C at constant cooling rate of 3 K/min, then the box was pushed into the water jacketed exit zone. At least three parallel samples each were tested as annealed. Then the die (shear) surfaces of the annealed samples were carefully dry ground with SiC grinding paper, in order to remove the springback and make them tightly fit into the die; the clearance to the die cavity was <0.1 mm. The ground bars were repressed at 600 MPa in the same tool previously used for powder pressing; once more, die wall lubrication was afforded. Three parallel samples each were tested as repressed. Finally, the remaining specimens were sintered in the high temperature zone of a high temperature, SiC rod heated push type furnace with gas-tight superalloy retort and remained there for 60 min at 1250°C in flowing N₂ of 99.999% purity. After sintering, the
box was pushed into the water-jacketed exit zone and cooled with a linearized cooling rate of approx. 0.5 K.s\(^{-1}\).

The annealed, repressed and sintered specimens were characterized by measuring the density through water displacement. In this case the density was determined by the Archimedes method (ASTM B311) since this technique is more precise than calculating the density from the dimensions and mass measurements as was done with the green compacts. Before Archimedes testing the specimens were surface impregnated using a commercial waterstop spray. The transverse rupture strength was determined according to ASTM B528, the distance between supports being 25.4 mm (1 inch), using a universal testing machine Zwick 1474. The test bars were about 8.5 mm thick; it should be noted that testing of such thick specimens with a span length of only 25.4 mm (1 inch) is not standard, and the results should thus be taken not as absolute values but to show the trends. The apparent hardness (macro hardness) was measured as Vickers hardness on an EMCO M4U-025 tester with a load of 30 kg (HV30), in the cross section of carefully sectioned and polished specimens. Microhardness measurement was done using a low load of 10 g and microscopic measurement of the indentations. Metallographic sections were prepared following standard procedures to make sure that the pore structure was properly shown. Etching was undertaken with a solution of 1% Nital. Fracture surface analysis was done on a scanning electron microscope JEOL 6400 in the secondary electron mode.

RESULTS AND DISCUSSION

Physical and mechanical properties

For studying the evolution of densification and properties, all manufacturing steps should be considered in a careful analysis, starting from pressing the metal powder in a die. Another attempt should be done to analyse changes in the compact taking place during presintering, repressing and sintering, respectively. Any characteristic change in each stage of fabrication is important for the final properties.

Also the response of characteristics to the manufacturing parameter may vary for each step. Although the trends may be similar, the changes of any properties are not equal. If the influence of each parameter is considered separately, the following equation could be supposed for describing any change on final characteristics:

\[
\frac{dC_r}{d(T_{1st})} d(P_{1st}) + \left( \frac{dC_r}{d(T_{ann})} \right)_{P_{1st}, T_{ann}} d(T_{ann}) + \left( \frac{dC_r}{d(P_{2nd})} \right)_{P_{1st}, T_{ann}} d(P_{2nd}) + \left( \frac{dC_r}{d(T_{sim})} \right)_{P_{1st}, T_{ann}} d(T_{sim})
\]

where \( C_r \) is the relative characteristic; \( P_{1st} \) is the first compacting pressure; \( T_{ann} \) is the intermediate annealing temperature; \( P_{2nd} \) is the repressing pressure and \( T_{sim} \) is the sintering temperature.

Accurate prediction of any characteristics is based on an understanding of the underlying effect of pressing, annealing, repressing and sintering. For instance, \( \left( \frac{dC_r}{d(T_{ann})} \right)_{P_{1st}} \) has been studied at constant pressing and repressing pressure in [13, 14] for Fe-Cr-Mo-C steel.

In the present investigation the influence of first compacting pressure on the evolution of properties in the DPDS process, i.e. \( \left( \frac{dC_r}{d(P_{1st})} \right) \), was investigated, and it is tried to clarify the effects.
The effect of the first compacting pressure on work hardening introduced and repressing response of Cr-Mo alloyed steel was evaluated on samples that were compacted at 200, 400 and 600 MPa, annealed at the same defined condition, repressed at uniformly 600 MPa and finally sintered at 1250 °C for 60 min in N2.

The properties after annealing, repressing and sintering, respectively, were determined. The obtained values are listed in Table 1 and, for better comparison and visibility of the trends, are also shown graphically in Fig.1. Figure 1a shows that with higher first compacting pressure, the density of the annealed samples increases significantly, which mirrors the compressibility curve.

Tab.1. Main properties of the annealed, repressed and sintered materials; (Intermediate anneal: 30 min at 850°C in N2 followed by cooling from 850°C to 601°C at cooling rate of 3 K/min; sintering 60 min at 1250°C in N2)

<table>
<thead>
<tr>
<th>Process</th>
<th>Compacting pressure</th>
<th>Archimedes density [g.cm⁻³]</th>
<th>TRS [MPa]</th>
<th>Apparent hardness Ferritic region</th>
<th>Microhardness HV0.01 Pearlitic/bainitic region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed</td>
<td>200</td>
<td>5.55</td>
<td>70</td>
<td>34</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>6.46</td>
<td>129</td>
<td>64</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>6.98</td>
<td>230</td>
<td>82</td>
<td>96</td>
</tr>
<tr>
<td>Repressed</td>
<td>200 + 600</td>
<td>6.97</td>
<td>134</td>
<td>118</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td>400 + 600</td>
<td>7.13</td>
<td>254</td>
<td>120</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td>600 + 600</td>
<td>7.26</td>
<td>300</td>
<td>123</td>
<td>167</td>
</tr>
<tr>
<td>Sintered</td>
<td>200 + 600</td>
<td>7.09</td>
<td>1282</td>
<td>203</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>400 + 600</td>
<td>7.26</td>
<td>1449</td>
<td>220</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>600 + 600</td>
<td>7.38</td>
<td>1562</td>
<td>240</td>
<td>---</td>
</tr>
</tbody>
</table>

Although the maximum repressed density was achieved by applying the highest first compacting pressure, not surprisingly the effect of repressing – described as the gain in density - was more pronounced for lower first compacting pressure (i.e. at lower green density) than with higher pressures; so that comparison of the density values indicates that the repressed parts are 25.6%, 10.4% and 4.0% denser than the annealed ones (relative to the density of the latter). Here, the higher residual porosity in samples compacted at lower pressure helps densification during repressing at 600 MPa.

The change of the repressed density can also be related to the removal of admixed graphite from the interparticle contacts. To some extent carbon is removed as CO/CO2, as a consequence of carbothermic reduction of oxides, see [13, 15-16], and at least in part it is dissolved in the matrix which process generates additional pore space and thus enables the green parts to be better compactible during repressing despite some increase of the microhardness. It seems that removal of graphite as CO/CO2 is enhanced in the samples compacted at lower pressure, in consequence of the presence of interconnected pores, while carbon dissolution in the matrix, which increase the microhardness, is less pronounced, which might be attributable to the less intense physical contact between metal powder particles and graphite flakes. Therefore the better compressibility of the softer matrix as well as the additional pore space generated by disappearance of graphite would be helpful for more densification after repressing. This effect should however be more pronounced for standard alloy systems such as Fe-Cu-C, Fe-Ni-Cu-Mo-C or Fe-Mo-C since for Cr-Mo
alloyed grades the main deoxidation processes occur rather above the annealing temperature applied here, at least in \( \text{N}_2 \) [15, 17].

After sintering, the density shows a very similar trend as after repressing, the levels being generally slightly higher, as a consequence of the high sintering activity of the Cr-Mo prealloyed powders, as described e.g. in [18-19].

The results of hardness measurement HV 30 for annealed, repressed and sintered samples are depicted in Fig.1b.

![Fig.1a-d. Effect of first compacting pressure on properties of annealed, repressed and sintered Fe-Cr-Mo-C. Compacted at 200/ 400/600 MPa, annealed 30 min at 850°C in \( \text{N}_2 \), repressed at 600 MPa, sintered 60 min at 1250°C in \( \text{N}_2 \).](image)

The influence of first compacting pressure on the hardness of uniformly annealed samples is clearly visible – as a consequence of the widely varying density - but after repressing at 600 MPa the differences are negligible. I.e. the hardness of repressed samples attains more or less the same level regardless of the first pressing, but in all cases higher than obtained after annealing. In any case, the quite significant contribution of work hardening introduced during repressing to the total hardness is clearly evident; at least for the lowest initial compacting pressure the hardness increase caused by repressing is as much as gained further on by sintering. For the higher first compacting pressure the relative effect of sintering increases, on one hand because of the higher final hardness caused by the higher density and on the other hand by the lower degree of deformation during repressing. This agrees well with results obtained in machining of sintered steels for which it has been shown that the pronounced work hardening by pore compression just in front of the cutting edge is the main reason for the poor machinability of PM steels [20].
The transverse rupture strength, which was measured here to reveal the mechanical strength of interparticle contacts, increases with higher first compacting pressure, as expected (Fig.1c).

For each first compacting pressure (i.e. green density level), repressing improves the TRS somewhat compared to the annealed samples. In this case of increasing TRS, the formation of additional pressing contacts by repressing seems to play the major role, as indicated by the fracture surfaces (see below).

Sintering causes a profound increase in repressed transverse rupture strength. This can be attributed to the formation of additional pressing contacts during repressing that are turned into sintering necks as well as to growth of the necks already present after intermediate annealing (see Fig.7). To some extent also the change of the pore connectivity may add to the higher TRS, since it has been shown that especially for Cr-Mo prealloyed steels closed porosity may become dominant already at density levels < 7.4 g.cm$^{-3}$ [19], and closed porosity means higher load bearing cross section for a given density level [21].

Fig. 1d shows the transverse rupture strength of specimens versus hardness. The dramatrical improvement of TRS by the final sintering compared to annealing and repressing, respectively, is clearly evident while the increase of the hardness is markedly less pronounced.

Here, in order to identify the underlying mechanisms taking place during each stage of the double-press-double-sintering (or, more correctly, press-anneal-repress-sinter) process, microstructure and fracture morphology were studied as described in the following.

**Metallographic investigations**

Metallographic investigation was performed to reveal the microstructural changes after each manufacturing step.

When studying the microstructure of specimens the main interest was focused on the extending and spreading of second microstructural constituents in the generally ferritic material, after annealing, repressing and sintering, respectively.

Three effects on the microstructure of annealed samples are obvious, in consequence of experiencing various work hardening influences through applying differing first compacting pressure;

- **Lattice-defect enhanced diffusion (carbon dissolution):** High first compacting pressure results in enhanced carbon transport, as a consequence of more lattice defects being present. This in turn results in a change of austenite nucleation in the ferritic matrix and in faster carbon dissolution (Fig.2a, b, c).

- **Recrystallization rate:** When more work hardening takes place, the rate of recrystallization will be increased in a specific annealing regime. The accelerated recrystallization as the result of first (powder) compacting at high pressure is demonstrated by comparing the micrographs of repressed samples at lower magnification (see Fig.3). Of course, recrystallization of the ferrite lowers the defect-enhanced transport described above; it is followed by ferrite-austenite transformation which generates a completely new lattice.

- **Pearlite distribution:** It is evident that in the annealed and the repressed specimens the distribution of the pearlite is inverse to what would be expected: pearlite is found at the cores of the grains and ferrite at the rim, although carbon definitely comes from the surface, and pearlite should therefore appear first at the rim. This effect has been described also otherwise [22, 23] and can be explained by assuming that at least part of the graphite has been dissolved in the matrix during annealing and was fairly evenly
distributed already when the carbothermic reduction of the surface oxides started which then consumed the near-surface carbon in the austenite lattice. In any case this pearlite distribution can be regarded to be beneficial for densification during repressing since the softer structure, ferrite, is at the sites of deformation during pressing.

Fig.2a-f. Microstructure and microhardness (HV0.01) of samples compacted at different pressures after annealing for 30 min at 850°C.

Fig.3. Microstructure and microhardness values (HV0.01) of samples compacted at different pressures, annealed at 850°C and repressed at 600 MPa.

The sintered structures are almost fully bainitic (Fig.4). The samples first compacted at lower pressure show slightly coarser bainite than those compacted at higher pressure. Some cracklike lines are indicated by arrows in the sintered structure of samples
first compacted at 200 and 400 MPa, but it is more probable that those are simply artifacts from polishing, indicating pores that have been partially closed. If cracks had been generated during repressing, in the fracture surfaces of the sintered specimens at least locally fracture morphologies would have been found as known to be caused by green cracks [24], which are however not visible here (see Chapter 3.3. below).

Comparing the micrographs of repressed samples with the annealed microstructure shows deformation of particles by repressing at 600 MPa (see in (Fig.3a, b, c) the increased number of grains in unit area).

Fracture surfaces

The fracture surfaces obtained from TRS test specimens give a good reference to the corresponding properties obtained after annealing, repressing and sintering, respectively.

When comparing the fracture surfaces of annealed samples (Fig.5) it is clear that the rate of recrystallization will be increased if more work hardening has been taken place at room temperature, because of higher driving force, and therefore higher density would be attained by repressing and also somewhat better interparticle bonding: The fracture surface of the annealed sample first compacted at 600 MPa shows some contact formation between the particles, a few dimples can be seen in the fracture surface (Fig.5c), while in the case of annealed samples which had been compacted at 400 MPa the contacts are extremely limited (Fig.5b) and for samples compacted at 200 MPa cannot be easily found (Fig.5a).

The fracture surfaces of repressed samples (Fig.6) show that the fracture occurred through the mechanical contacts generated during first pressing and those newly created
after repressing, and the broken necks that had been generated during annealing only can be observed as a few dimples in Fig. 6c.

![Fig.6. Fracture surface of specimens compacted, annealed at 850°C and repressed at 600 MPa; broken TRS test bars.](image)

The fracture surfaces of sintered samples differ from those of annealed and repressed specimens insofar as the distinct boundaries between the original powder particles are no more visible, i.e. the powder particles cannot be identified any more, which is the usual indicator for sound interparticle bonding. Furthermore, after 600 MPa first pressing there is considerable transgranular cleavage fracture, which indicates that the sintering necks are no more the weakest areas in the sintered body; also this shows very good sintering effect (Fig. 7) and can be regarded as an indicator for the explained trend in Fig. 1d.

![Fig.7. Fracture surface of specimens compacted, annealed at 850°C, repressed at 600 MPa and sintered 60 min at 1250°C; broken TRS test bars.](image)

**CONCLUSIONS**

Optimized Double Press Double Sintering (DPDS) process is regarded as a promising method for improving physical and mechanical properties of Cr-Mo prealloyed sintered steel. In this procedure, carbon dissolution during first sintering (in fact a presintering / annealing treatment) plays a major role to change repressibility (and densification during repressing, consequently). Besides the intermediate annealing temperature [13], the first compacting pressure has a significant influence on carbon dissolution and thus on the fraction of pearlite generated after annealing. Enhancement of first compacting pressure encourages carbon diffusion by providing short-circuit diffusion in consequence of accelerated recrystallization, and offers significant advantage in obtaining improved physical and mechanical properties. A specific feature of the Cr-Mo prealloyed steels is the emergence of an “inverse” core-rim structure after annealing, with ferritic rim and pearlitic core, contrary to what would have been expected since carbon comes from the particle surfaces, i.e. a pearlitic
rim would have been regarded more probable. This “inverse” structure indicates that
carbothermic reduction of the surface oxides occurs after carbon dissolution; in any case,
softer rim areas mean that the areas most heavily deformed during repressing are the more
ductile ones which should help densification.

The study of metallographic sections and fracture surfaces gives a good reference to
the explained mechanism taking place during each stage of fabrication. The finest grain
structure and the extended diffusion zone in the micrograph of sample compacted at the
highest pressure after annealing as well as the neck formation between the particles in its
fracture surface is strong evidence for accelerated recrystallization and carbon dissolution
which occur in highly work hardened state.

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