STUDY ON THE INTERPARTICLE BONDING OF DOUBLE PRESSED PM ALLOY STEELS

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Abstract
Double pressing is a common technique for improving the relative density of sintered steel components, with resulting beneficial effect on the mechanical properties. To eliminate the work hardening introduced by the first pressing, an intermediate anneal is done before the second pressing, typically at temperatures at which carbon is not yet dissolved. In this work, interparticle bonding caused by the intermediate anneal is described through fractographic techniques for prealloyed steels Fe-Mo-C and Fe-Cr-Mo-C and compared to the fracture surfaces after final sintering. It showed that after annealing, interparticle bonding is significantly more pronounced in the Mo alloyed steel than in the Cr-Mo grade, apparently as a consequence of the more stable surface oxides in the latter material. After final sintering however there are virtually no differences and with regard to mechanical properties the Cr-Mo material offers considerable advantages.

Keywords: sintered steels, double pressing, presintering, interparticle bonding

INTRODUCTION
High relative density, i.e. low porosity, has been the goal of powder metallurgy parts production since it started in the 1930s. The reason is the relationship between density and mechanical properties [1,2]; furthermore, components which, as a consequence of sufficiently high density, contain closed pores are easier to handle in many secondary operations.

In contrast to e.g. ceramics or hardmetals, densification during sintering is usually not desirable for PM precision parts (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. Here, the main obstacle against densification is the work hardening of the bulk powder during pressing which at least at ambient and near-ambient temperatures prevents attaining full density. For ferrous PM parts about 7.1 g·cm⁻³ are regarded as the maximum in industrial practice. Techniques such as warm compaction, high velocity compaction or high pressure compaction have been introduced; nevertheless, one of the most common methods to attain density levels above the usual levels is still double pressing. In this case the work hardening is eliminated by an intermediate annealing treatment, and in a second pressing step the compacts can be densified to levels up to 7.4 g·cm⁻³.

Generally it is assumed that carbon-containing steel compacts should be annealed at temperatures at which the carbon – usually admixed graphite - is not yet dissolved in the

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matrix, to avoid unwelcome hardening effects. On the other hand, it should not be ignored
that graphite takes a considerable volume of the compact, thus inhibiting densification. In
[3] it has been shown that for alloy steels there is an optimum annealing temperature which
results in maximum repressing effect. In the present work, the effect of repressing on the
fracture behaviour of the repressed as well as of the finally sintered materials is described.

EXPERIMENTAL PROCEDURE
Prealloyed powders Astaloy CrL (Fe-1.5%Cr-0.2%Mo) and Astaloy Mo (Fe-1.5%Mo), respectively, were mixed with 0.6%C (natural graphite UF4), and the mixes were
uniaxially compacted at 600 MPa to bars with rectangular shape (55x10x10 mm³) in a
pressing tool with floating die, the green density then being measured through the
dimensions. These samples were annealed/presintered in a tube furnace for 30 min at
various temperatures (400, 500, 600, 700, 750, 800, 850, 900, 950, 1000°C) in flowing N₂
of 99.999% purity and cooled in the water jacketed exit zone (cooling rate ≅ 36 K/min).
After grinding the die (shear) surfaces of the samples (to compensate for springback and
make them fit into the die), they were repressed at 600 MPa in the same tool previously
used for powder pressing. At least three parallel samples each were tested as repressed.
Finally, the remaining specimens were sintered for 1 hr at 1250°C in flowing N₂ of 99.999
purity, cooling being afforded once more in the water-jacketed exit zone of the furnace.

The repressed as well as the sintered specimens were characterized by measuring
the density through water displacement. The transverse rupture strength was determined in
3-point bending, the distance between supports being 25.4 mm, using an universal testing
machine Zwick 1474. The apparent (= macro-) hardness was measured on an EMCO M4U-
025 tester and the microhardness on a LECO LM100. Impact testing was done on a
Wolpert tester with Wₘₐₓ = 300 J, the bars being tested in the unnotched condition.
Metallographic sections for optical investigation were prepared following standard
procedures; to make sure that the pore structure was properly shown, the specimens were
resin impregnated before polishing. Fracture surface analysis was done on a scanning
electron microscope Jeol 6400 in secondary electron mode.

MECHANICAL PROPERTIES
In [3] it has been shown that both for Fe-Mo-C and Fe-Cr-Mo-C a “window” for
the annealing temperature can be defined within which the amount of carbon dissolved is
still too small to exert a significantly adverse effect on the compressibility while being
sufficiently high to generate empty space to compress. In Figure 1 the repressed density, the
transverse rupture strength and the macrohardness are shown as a function of the annealing
temperature in the range 700 … 1000°C; it is clearly visible that although the hardness of
the materials increases significantly at temperatures above 700°C, as shown in [3], the
repressed density attains its maximum after annealing at about 800°C. In this case the
hardness is still moderate, at least for the Cr-Mo alloyed steel which also shows the higher
repressed density. However, annealing at 900°C results in a marked drop of the density,
indicating that between 800 and 900°C the increase of the hardness is more due to carbon
dissolution than to formation of interparticle contacts which can be expected to dominate at
the lower temperatures, as indicated by the transverse rupture strength.
Fig. 1. Properties of repressed Fe-Mo-C and Fe-Cr-Mo-C as a function of the annealing temperature. Compacted 600 MPa, annealed 30 min in N\textsubscript{2}, repressed at 600 MPa.

Fig. 2. Properties of repressed and then sintered Fe-Mo-C and Fe-Cr-Mo-C as a function of the annealing temperature. Compacted 600 MPa, annealed 30 min in N\textsubscript{2}, repressed at 600 MPa, sintered 60 min at 1250°C in N\textsubscript{2}.
After sintering (Fig.2), the density shows a very similar trend as after repressing, the levels being generally slightly higher. The impact energy, which was measured here to reveal the mechanical strength of the interparticle contacts, follows the same pattern; however it can be seen that the IE values obtained with the Cr-Mo alloy steel are markedly higher than those measured on the Mo alloyed grade. This supports Chen Xu’s findings [4] that in the as-sintered state, the finer microstructure of the Cr-Mo material is superior to the relatively coarse upper bainite typical for the Mo alloyed steels. Surprisingly, in the case of the Cr-Mo alloyed steel the effect of the annealing – which means of the density – on the hardness is less pronounced than for the Mo alloy grade. In any case, the fact that the impact energy follows more or less the same trend as does the density indicates that damage during repressing – microcracks etc. formed through rupturing of sintering necks generated during annealing – did not play a role here; otherwise, the impact energy at least in the repressed state should drop at lower annealing temperatures than the density.

FRACTURE SURFACES AS-REPRESSED

In Figure 3 typical fractographs of repressed specimens that have been annealed at different temperatures are shown. It is clearly visible that for the Mo alloyed grade, the first indication of neck formation is found in those specimens that have been annealed at 800°C (see Fig.3b). Small areas containing dimples can be seen that are localized and extremely small at 800°C but tend to form larger areas containing coarser dimples at 900°C.

For the Cr-Mo alloyed steel, in contrast, there are virtually no dimples visible at 800°C, and also at 900°C areas where plastic deformation can be identified are extremely rare. This would indicate that at moderate temperatures, formation of sintering necks is significantly slower in the Cr containing steel, which agrees with the findings e.g. of Kremel et al. [5] and is also supported by the lower transverse rupture strength observed with these materials at each annealing temperature. The reason for the slower response to the (pre)sintering treatment can be found in the more stable oxide layers covering the Cr-Mo steel particles which require significantly higher temperatures for reduction, at least for carbothermic reduction in inert atmospheres (in H₂, at least partial reduction occurs at lower temperatures [6]).

In principle it might be assumed that the faster formation of sintering necks in the Mo alloy steel is an advantage; on the other hand, it should not be ignored that sintering necks that have been formed but are then ruptured during repressing might be the nuclei for microcracks. In any case, the ductility of as-annealed steels is so low that any significant tensile forces applied during repressing will result in cracking anyhow; it cannot be expected that the slightly higher transverse rupture strength of the Mo alloy steel will make any difference in that respect.

If the relatively homogeneous distribution of the dimple-containing areas shown in Figs.3b and 3c can be taken as an indicator that cracking during repressing has not occurred here is a matter of discussion; it might be assumed that cracking due to overloading during repressing, possibly as springback effects, would result in different fracture morphology than the loading in the case of static bending tests. Real repressing cracks should be clearly discernible after sintering, since in these areas there should be no dimples at all, and the fracture surfaces should resemble the smooth ones typical for parts with green cracks.
Fig. 3. Fracture surfaces of repressed Fe-Mo-C and Fe-Cr-Mo-C as a function of the annealing temperature. Compacted 600 MPa, annealed 30 min in N$_2$, repressed at 600 MPa.

FRACTURE SURFACES AS-SINTERED

The as-sintered fracture surfaces differ from the repressed ones insofar as the original powder particles are no more visible, which can be regarded as an indicator for sufficient interparticle bonding. A further indicator is the emergence of transgranular cleavage fracture, which is virtually absent with the repressed specimens, in which case fracture occurs exclusively at the relatively small sintering contacts, i.e. the deformation and fracture processes are very much localized. Cleavage tends to become more frequent with increasing annealing temperature, which is not surprising since it is well known that in sintered steels, cleavage is promoted by higher density levels (e.g. [7,8]).
Fig. 4. Fracture surfaces of repressed and then sintered Fe-Mo-C as a function of the annealing temperature. Compacted 600 MPa, annealed 30 min in N\textsubscript{2}, repressed at 600 MPa, sintered 60 min at 1250°C in N\textsubscript{2}.

Fig. 5. Fracture surfaces of repressed and then sintered Fe-Cr-Mo-C as a function of the annealing temperature. Compacted 600 MPa, annealed 30 min in N\textsubscript{2}, repressed at 600 MPa, sintered 60 min at 1250°C in N\textsubscript{2}. 
When comparing the fracture surfaces of the Mo and Cr-Mo alloyed steels (Figs. 4 and 5), it is evident that the former material exhibits significantly more cleavage facets than the Cr-Mo alloyed variant. This becomes particularly evident when studying the materials annealed at 500°C: here, the Mo alloyed variant shows quite significant cleavage (Fig. 4c) while in the Cr-Mo steel virtually exclusively dimple facets are shown. Since the density of the materials is not too different, it can be concluded that also here the finer microstructure of the Cr-Mo variant is less prone to promote cleavage than the coarse upper bainite typical for as-sintered Mo steels. The more ductile fracture behaviour of the Cr-Mo type can also be regarded as the reason for the significantly higher impact energy of this material for each annealing condition.

CONCLUSIONS

From the results presented here can be concluded that repressing of Mo and Cr-Mo alloyed PM steel compacts after intermediate annealing is an effective way to attain high density levels. The optimum annealing temperature is at about 800°C, i.e. at relatively high temperatures at which some carbon dissolution already can be expected. This is however not as unwelcome as frequently assumed since the voids left by the dissolved graphite can be densified during repressing, in contrast to the remaining graphite. At higher annealing temperature, however, the density drops, indicating that in this case the “hardening effect” overcomes the “volume effect” while at 800°C these effects are neatly balanced.

The fracture surfaces of the repressed specimens indicate that in the Mo alloyed steels there should be stronger interparticle bonding, indicated by the emergence of dimples in the broken sintering necks, which are not visible in the Cr-Mo steels. This is to some extent supported by the transverse rupture strength data, which are higher for the Mo steels compared to the Cr-Mo grades. However, the difference is significantly smaller than would be expected from the fracture surfaces, which confirms that fractographic studies only are not sufficient for describing the mechanical behaviour but that also the mechanical properties have to be considered.

In the as-sintered state, at least after high temperature sintering as employed here, the Cr-Mo alloy steels shows markedly better properties than the Mo alloyed grade, in particular better impact energy values combined with higher hardness. That both properties are better might indicate that the sintering effect is more beneficial here, which is in agreement with previous studies on Cr-Mo alloyed steels. The impact fracture surfaces however reveal that there is also less tendency to cleavage fracture: while the Mo alloyed steels show cleavage already in the specimens intermediate annealed at 500°C and still more in case of annealing at 800°C – in which case the higher density can be expected to promote cleavage - , in the Cr-Mo alloyed steels there is virtually no cleavage for 500°C and only fairly localized transgranular facets even for the highest density levels attained. This once more confirms that at least in the as-sintered state, the microstructure of Fe-Cr-Mo-C is more favourable regarding the mechanical behaviour than is that of Fe-Mo-C.

REFERENCES