CHANGES IN DIMENSIONS AND MICROSTRUCTURE OF COMPACTS FROM COPPER-COATED IRON POWDERS DURING SINTERING

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Abstract
Unlike compacts from elemental Fe and Cu powders, compacts from Cu-coated Fe powders are not expected to swell upon sintering because Cu need not penetrate the inter-particle contacts. To verify this, iron powder particles were coated with a copper by cementation, compressed into cylindrical compacts and sintered either in a furnace (875°C, 1020°C, 1120°C) or in a dilatometer (1120°C). Compacts sintered at 875°C reduced both height and diameter, while those sintered at 1020°C and 1120°C showed decrease in height and increase in diameter. Dilatometry revealed that the height and diameter behaved differently if a green cylindrical compact was sintered, while they varied similarly throughout the re-sintering. Microstructural investigation found a free copper at grain boundaries in samples sintered at 875°C. In samples sintered at 1120°C, the whole amount of copper (3 wt%) was dissolved in iron and microgradients in composition were created. To explain observed dimensional changes qualitatively, it was supposed that (i) the coating layers contain copper oxides, and (ii) coatings in lateral contact regions are worn during compaction. If heated, the compact tends to remove oxygen and to restore uniform coatings. This irreversibly affects the compact’s dimensions.

Keywords: powder metallurgy, Cu-coated Fe powder, compaction, sintering

INTRODUCTION
Properly heat-treated parts made from iron and copper powders exhibit better mechanical properties than products sintered from a pure iron [1]. But the dimensions of sintered compacts are usually larger than those of green compacts.

The specific energy of a free iron surface exceeds the sum of specific energies of the iron-copper interface and the free surface of copper melt. So, to reduce the overall energy the system undergoing sintering tends i) to remove the free iron surfaces and ii) to minimize the free copper surface. To do this, the molten copper i) penetrates contacts between iron particles, and ii) nearly uniformly covers iron particles. This penetration of a copper into interparticle contacts causes the compact to swell [2-4].

If one uses a powder consisting of iron particles coated with a copper, the copper need not penetrate the contacts. So, it is expected that such compacts do not enlarge upon sintering.
To verify this assumption, iron powder was coated with 3wt% of copper by cementation. Powders obtained were compacted into cylindrical samples and sintered at temperatures of 875°C, 1020°C and 1120°C. An expected shrinkage was observed only for samples sintered at 875°C. For other sintering temperatures, the samples shrunk parallelly and swelled perpendicularly to the compaction direction.

To obtain further details about how the compact behaves, the sintering in a dilatometer was also carried out.

The results of an investigation of how the process of sintering affects dimensions and microstructure of compacts from copper-coated iron powders are presented in this contribution.

EXPERIMENTAL

Water-atomized iron powder, Höganäs ASC 100.29 grade, fraction 63-180 μm, was used as a starting raw material. Part of this powder was utilized for reference pure iron samples, the rest was coated.

To realize coating, the powder was put into an aqueous electrolyte which contained coppersulfate and sulphuric acid. The resultant copper amount was controlled by the coppersulfate content in the electrolyte. After stirring several minutes, copper layer was deposited on surfaces of iron particles by cementation process. More details of the fabrication and characteristics of the powders were presented elsewhere [1].

The oxygen content of powders was analysed. The combustion of a small portion of powder in a graphite crucible produced the CO gas, which was transported into a measuring chamber via helium as a carrier gas and quantified by means of an infrared detector [5].

The powders obtained were cold pressed into cylinders 10 mm in diameter and with heights of about 10 mm. The compaction pressure was 600 MPa. The lubricant was not added to the powder, zinc stearate was used as a die wall lubricant. Compacts were sintered in Marsch laboratory furnace under the following conditions: sintering temperatures were 875°C, 1020°C and 1120°C, time was 60 minutes, atmosphere 90%N₂ - 10%H₂.

Dilatometric sintering was carried out in a horizontal pushrod dilatometer Netzsch DIL 402C. The compact’s dimensions parallel and perpendicular to the pressing direction were measured. Pure hydrogen (5.0 quality) was used as the sintering atmosphere. Heating and cooling rates were 10°C/min. Isothermal sintering was carried out for 60 minutes at 1120°C.

The reference samples from a pure iron powder were compacted, sintered and examined in the same way as the samples from coated powders.

Dimensions of both green compacts and sintered samples were measured with a micrometer calliper (+0.01 mm). Dimensional changes were evaluated. The compacts were weighed with an accuracy of ±0.001 g.

For metallographic examinations the samples were cut, mounted, ground, polished and nital etched. The microstructure of the samples was analysed by a light optical microscope (OLYMPUS GX71, Japan).

RESULTS AND DISCUSSION

For the used copper concentration (3 wt.%), the particle surfaces were almost completely covered with a copper, which let the powders appear copper-coloured.

The oxygen content of the reference iron powder was found to be 0.072 wt.% and that of the coated powders 0.269 wt.%.
Microstructure

Metallographic examination of microstructure demonstrated that only a small amount of Cu was dissolved in iron after sintering at the temperature of 875°C (well below the copper melting point). Free copper is observed on the particle’s boundary (Fig.1a).

After sintering at 1020°C (slightly below the copper melting point), there is still possible to find a “free” copper on the boundary of original iron particles. But we can already see a copper that has diffused into volume of iron (Fig.1b).

As regards the sintering at temperature of 1120°C (slightly above the copper melting point), sintered samples reveal a microgradient structure (Fig.1c). The cores of original iron powder particles are unaffected (bright) and the regions around, consisting of the Fe-Cu solid solution, are attacked by the etching reagent (dark). Copper is entirely dissolved in iron particles.

![Fig.1](image1.png)

Fig.1. Structure of samples coated with 3wt.% of Cu and sintered at temperatures of a) 875°C, b) 1020°C, c) 1120°C, nital etched.

Overall dimensional changes of cylindrical samples

Upon sintering, the compacts from Fe powders shrank in every direction and compacts from mixed Fe and Cu powders swelled in every direction (Table 1). Compacts from coated powders behaved in a similar manner as pure Fe compacts if sintered at 875°C - all cylinders contracted in all directions and their densities slightly increased. But the response to sintering at 1020°C and 1120°C was different from that of pure Fe compacts as well as from that of mixed Fe-Cu compacts. Samples shrank in height (in the direction parallel to the compaction direction) and swelled in diameter. The density of these samples slightly decreased. Typical dimensional changes upon sintering are shown in Table 1.

Tab.1. Density and dimensional changes of compacts from the tested materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Green density [g.cm⁻³]</th>
<th>Sintering temperature [°C]</th>
<th>Change of density Δρ/ρ [%]</th>
<th>Change of height Δh/h [%]</th>
<th>Change of diameter ΔΦ/Φ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe coated with Cu (3 wt.%)</td>
<td>7.114</td>
<td>875</td>
<td>+0.267</td>
<td>−0.276</td>
<td>−0.051</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1020</td>
<td>−0.125</td>
<td>−0.318</td>
<td>+0.110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1120</td>
<td>−1.545</td>
<td>−0.049</td>
<td>+0.562</td>
</tr>
<tr>
<td>Fe mixed with Cu (3 wt.%)</td>
<td>7.119</td>
<td>875</td>
<td>+0.269</td>
<td>−0.148</td>
<td>−0.048</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1020</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1120</td>
<td>−2.335</td>
<td>+0.060</td>
<td>+1.061</td>
</tr>
<tr>
<td>Fe</td>
<td>7.076</td>
<td>875</td>
<td>+0.271</td>
<td>−0.159</td>
<td>−0.095</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1020</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1120</td>
<td>+0.321</td>
<td>−0.291</td>
<td>−0.128</td>
</tr>
</tbody>
</table>
Dilatometric investigation of cylindrical samples

To obtain reference data, plain iron compacts were studied in a dilatometer first. Typical results of this investigation are presented in Fig.2. One can see that there is no remarkable difference between dimensional changes measured in directions parallel and perpendicular to the compaction direction. Interesting asymmetry in $\alpha\rightarrow\gamma$ and $\gamma\rightarrow\alpha$ transitions [6] is not addressed in this contribution.

![Fig.2. Dilatometer graphs for iron compacts measured parallel and perpendicular to the pressing direction.](image)

An example of dilatometric plots for compacts from Fe coated with 3 wt% of Cu is in Fig.3. It is evident that the sample’s height and diameter behaved dissimilarly throughout the first sintering, i.e. sintering of green compact (first run, Fig.3a). For the re-sintering, i.e. repeated sintering (second run, Fig.3b), the difference between sample responses in directions parallel and perpendicular to the compaction direction was found negligible if compared with the first sintering (first run).

![Fig.3. Dimensional changes of compacts from copper-coated iron powder (Fe+3wt.%Cu) measured in dilatometer in two directions: parallel and perpendicular to pressing direction. a) The first run; initial, first sintering of green compacts, b) second run; re-sintering – sintering of already sintered sample.](image)
One can see that the difference between radial and axial strains increases during the whole sintering process (though with a different rate). There are several stages within this process where the difference “skips”.

**DISCUSSION**

Such behaviour could result from the broken uniformity of coatings caused by the process of compaction.

There is an experimental evidence [7] that the powder mass undergoing uni-axial die compaction moves more near the central axis and the axial movement decreases from the axis towards the die wall. This means that a typical powder particle moves axially with respect to its surroundings. The relative motion leads to the sliding wear of adjacent surfaces (e.g. [8]).

Hence, the coatings in contact areas parallel to the compaction direction can get thinned or entirely removed during powder compaction. Wear debris and folds of coating are entrapped within pores near these contacts (Fig.4). Deformation of coatings in contacts perpendicular to the compaction direction is considered negligible.

![Fig.4. Compacted iron powder particles coated with 3wt.% of copper; compacting pressure of 600 MPa, LOM.](image)

If the compact gets hot it undergoes thermal expansion. At the same time, oxides contained in coating start to reduce. Removing the oxygen shrinks the sample’s dimensions. The thicker the layer of oxides that are reduced, the greater the dimensional change. Hence, this process should reduce mainly the compact’s dimension parallel to the compaction direction. Dimensional changes resulting from thermal expansion and reduction shrinkage are thus anisotropic and irreversible, but they still preserve the non-uniformity in coating thickness. After reduction, iron grains remain coated with a copper.

The thermal expansion above $\alpha \rightarrow \gamma$ transition is more pronounced than that below transition due to higher expansion coefficient of austenite compared to ferrite and a higher diffusion of Cu into iron. At 1086°C (melting point of copper), the increase in expansion is caused by the liquid phase appearance (Fig.3 – 1. run). The difference between deformations in diameter and height slightly increased. It is supposed that if the compact is heated near to copper melting point, the mobility of copper atoms is remarkably increased, and the copper tries to minimize the surface energy and so to restore the uniform thickness of coating. This restoration causes the compact to swell. As the thickness of coatings was reduced primarily in lateral contacts, the compact tends to swell primarily laterally. However, simultaneously with the motion along the grain surfaces, the copper diffuses into
the iron particles. It depends on the rates at which the copper moves along and across the particle surface whether or not it will succeed in penetrating into worn contacts. The occurrence of liquid phase strongly accelerates motion along surfaces and raises chances that a sufficient amount of copper will reach the contact regions.

During the period of isothermal sintering, continuous shrinkage with a gradually decreasing rate is observed. It may reflect the fact that once the penetration of copper into contact region is complete, a more gradual densification process prevails due to a grain rearrangement, contact flattening, particle coarsening, etc. The initially swelled compact starts to shrink [9]. This reduces sample axial dimension and offsets a part of lateral swelling.

Cooling stage is characterised by thermal contraction with an allotropic transformation of iron. Again, the difference between diameter and height deformations slightly increases. Probably, the copper still penetrates into contacts. This process results in a practical uniformity of coatings and thus the system becomes more or less quasi-isotropic. As the oxides and different coating thickness are irreversibly removed, from this stage the dimensional changes are practically the same in the both directions and dilatometric curves are practically similar in the following stage of cooling as well as during the repeated sintering (Fig.3b).

CONCLUSION

Copper was deposited on a surface of iron powders by cementation until its concentration reached 3 wt%. Coated powders were pressed into cylindrical samples and sintered either in a furnace at temperatures of 875°C, 1020°C and 1120°C or in a dilatometer. Reference samples from a pure iron powder were prepared and tested in the same way.

Upon sintering at 875°C, all compacts contracted in every direction. The response of samples to the sintering at 1020°C and 1120°C was different. While compacts from iron powders shrank in all directions, the compacts from coated powders shrank in the direction parallel to the compaction direction (the height of cylinders) and swelled in the direction perpendicular to that (the diameter of cylinders).

Dilatometry revealed that the axial strain and radial strain of a cylinder compacted from pure iron changed almost identically during the whole cycle. The results for cylinders from coated powders depended on whether a green sample or already sintered sample was studied in a dilatometer. Re-sintering of already sintered samples provided results similar to those for reference samples - the height and diameter varied similarly. If a green compact was used, dilatometry data on the change in height evidently differed from those concerning the diameter.

To explain this anisotropy qualitatively, it was proposed that the coating consists of copper and copper oxides and that the coating is thinner in the contact areas parallel to the compaction direction than in contact areas perpendicular to that. The different coating thickness is the result of the character of motion of the powder mass during uniaxial die compaction.

The reduction of oxides and the tendency of copper to restore the uniform coating thickness can lead to observed phenomena. The mentioned irreversible processes are combined with reversible ones (e.g. anisotropic and nonuniform thermal expansion). The reversible changes are removed when the system is cooled back to the original temperature and do not contribute to the final dimensional changes.

The initial conditions (oxides, coatings with a different thickness…) that allow the above irreversible processes are removed during first, eventually second, sintering cycle.
Thus, the re-sintering would provide different data, qualitatively similar to those for reference sample.

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REFERENCES