

ON THE UNUSUAL DIMENSIONAL RESPONSE OF COMPACTED COPPER-COATED IRON POWDERS TO SINTERING

M. Kupková, M. Kupka, S. Strobl, C. Gierl, J. Wagesreither

Abstract

Compacted mixtures of iron and copper powders swell upon liquid phase sintering. An enormous expansion limits the use of such materials for more precise parts. The compacts are growing due to a penetration of molten copper into boundaries between iron grains. No swelling is therefore expected for compacts from coated powders as each of the iron particles is surrounded with copper in advance of sintering.

Samples from copper-coated iron powders were compacted and sintered. Though the compacts shrank in the compaction direction, they surprisingly swelled in directions normal to the compaction direction.

To explain this, a possible mechanism is proposed: Contacts parallel to the compaction direction are worn by the sliding of adjacent particles. This sliding arises due to a non-uniform axial movement of a powder mass undergoing closed die compaction. Worn coatings are restored by penetrating melt during sintering. Quick restoration of nearly uniform coating thickness swells the compact laterally. A succeeding densification process shrinks the sample along the compaction direction and also offsets a part of the lateral swelling.

Keywords: *sintering, copper coatings, iron, grain boundary wetting, swelling versus shrinkage*

INTRODUCTION

Iron-based alloys rank among the most widely utilised materials in powder metallurgy, and copper represents one of the most attractive and commonly used alloying elements. There are good reasons for this – an acceptable cost, easy production of copper powders, insensibility to oxidation, and satisfying properties of final products. After the proper heat treatment, sintered iron-copper alloys show higher mechanical properties than a pure sintered iron. In addition, the presence of a low melting-point phase offers an advantageous formation of the liquid. Liquid phase sintering or transient liquid phase sintering activate necessary densification processes and make the homogenisation of samples much faster.

With all these benefits, the formation of liquid phase also triggers an adverse process. The main disadvantage of compacts from blended iron and copper powders is that the copper-rich melt causes a swelling of compacts. The enormous expansion limits the use of this type of sintered steel for more precise parts.

That is why such mixed-powder compacts sintered at temperatures above the copper melting point have been studied for many years. It has been shown [1-3] that the compacts expand predominantly due to a transfer of liquid copper from its initial sites into

Miriam Kupková, Institute of Materials Research, Slovak Academy of Sciences, Košice, Slovakia

Martin Kupka, Institute of Experimental Physics, Slovak Academy of Sciences, Košice, Slovakia

Susanne Strobl, Christian Gierl, Jochen Wagesreither, Institute of Chemical Technology of Inorganic Materials, TU Vienna, Vienna, Austria

the contact areas between iron particles, Fig.1. The penetration of the copper-rich melt is rapid. It usually takes only a few minutes immediately after the liquid phase forms. Secondary pores are left at the copper original positions, Fig.2. If the compact is further held at the peak temperature, more gradual processes that increase the compact density begin to reveal themselves (grain rearrangement, contact flattening, particle coarsening, etc.). The initially swelled compact starts to shrink.

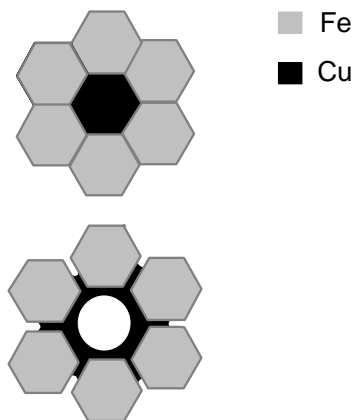


Fig.1. Schematic illustration of how the mixed-powder compact swells. The molten copper leaves its original sites and penetrates into boundaries between iron grains. Secondary pores are left at the copper original positions. The figure presents a state of compact before (the top part) and after (the bottom part) the liquid phase forms.

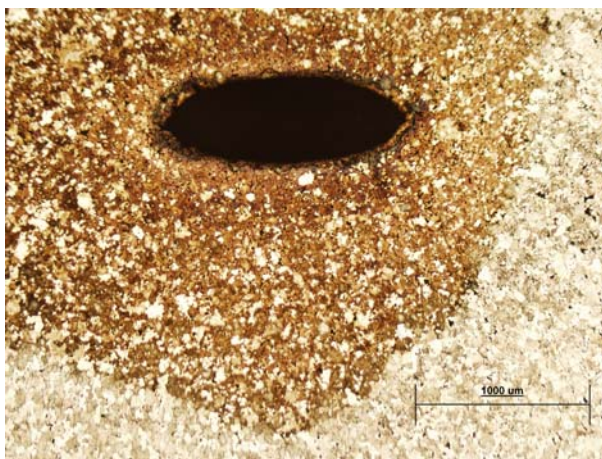


Fig.2. A hole left at the position of copper wire after the molten copper penetrated into the iron-powder matrix. A copper wire (0.5 mm in diameter) was put into an iron powder and the system was compressed at 600 MPa. The compact was sintered at 1120°C for 60 minutes. The darker area represents the copper-infiltrated region (nital etched, optical image).

A model that fairly quantifies expansion of mixed-powder compacts was proposed in [4]. That model was established on the premise that the amount of volume growth of a compact is equal to the volume of liquid copper which penetrates into iron inter-particle

boundaries. But this volume is not equal to the entire amount of copper available within the sample. Before the penetration begins, some amount of copper is consumed by diffusion during heating, some is consumed by filling the pores close to the original copper particles and pores on the surface of iron particles, etc. The succeeding shrinkage is not considered in [4].

In specimens compacted from iron powders coated with copper, the layer of copper is already sandwiched between each two neighbouring iron particles. So, as the main step of swelling is taken in advance during preparation of raw powders, the shrinkage of such compacts should be expected upon sintering.

As a justification for this expectation, behaviour of the fine-grain iron-copper composites can be mentioned. The composite granules were prepared through mechanical alloying by grinding the metal powders in a high-energy mill. The internal structure of the resultant granules contained alternating very thin iron and copper layers. Specimens compacted from such granules shrank upon liquid phase sintering [5].

The present study of dimensional changes of coated-powder compacts was initiated as a partial task of a wider programme aimed at mapping the properties of sintered steels with locally controlled gradients in composition. Iron-based powders were coated with different amounts of copper by cementation. Various bar-shaped and cylindrical samples were compacted from such powders and sintered above the copper melting point. A paradoxical finding was that the expected shrinkage of samples was observed only in the direction parallel to the compaction direction, whereas the swelling occurred in directions perpendicular to the compaction direction.

To gain some insight into such an unexpected anisotropy in dimensional changes, the following mechanism is proposed and discussed. Due to a non-uniform axial movement of a powder mass during closed die compaction, neighbouring particles slide against each other. As a result, the coatings are worn or even removed from inter-particle contact areas parallel to the compaction direction. The coatings are again re-established during subsequent sintering. This restoration of the more or less uniform covering of particles leads to a lateral swelling of compacts considered. The succeeding ordinary densification process reduces the compact dimension along the compaction direction and offsets a part of the lateral swelling.

Preliminary theoretical estimates for swelling amplitudes based on the above model are consistent with experimentally observed ones.

EXPERIMENTAL

An investigation of dimensional changes of sintered compacts from coated powders represents part of a more comprehensive programme aimed at investigating the properties of sintered steels with controlled heterogeneity in composition. The preparation of coated powders and test specimens were described elsewhere [6,7]. Hence, the manufacturing is only briefly sketched here, and just experimental data relevant for the problem considered are emphasised.

As a starting raw material, water-atomised iron powder was used, namely Höganäs ASC 100.29 grade. The fraction 63-180 μm was chosen. For reference compacts from mixed iron and copper powders, electrolytic copper FM by Ecka Granulate was utilised.

The iron powder particles were coated with different amounts of copper (3 and 8 wt%). To realise this, the iron powder was put into an aqueous electrolyte containing copper sulphate and sulphuric acid. The required resultant copper amount was controlled by the content of copper sulphate in the electrolyte. After stirring several minutes, the required

copper layer was deposited by the cementation process on the iron particle surfaces. For both copper concentrations, particle surfaces were almost completely covered with copper.

The powders investigated were compressed into test-bar and cylindrical shapes under pressure of 600 MPa. Bar-shaped compacts were sintered in pusher furnaces under the following conditions: sintering temperature 1120°C, time 60 minutes, atmosphere H₂. De-waxing conditions were 600°C, 30 min, N₂. Cylinders were sintered in a silit furnace under the following conditions: sintering temperature 1120°C, time 60 minutes, atmosphere 90% N₂ +10% H₂.

Dimensions of green compacts were measured. For green test bars, the length ranged from 55 to 100 mm, width from 5 to 12 mm, and powder-dependent height from 4.5 to 9.2 mm. For cylindrical specimens, the diameter was 10 mm and the height about 10 mm. Sintered samples were measured too, and dimensional changes were evaluated. Typical examples of dimensional changes are shown in Tables 1 and 2.

As expected, compacts from a pure iron contracted in all directions and compacts from mixed iron and copper powders swelled in all directions (Table 1).

Tab.1. Dimensional changes of compacts from pure iron powder and mixed iron and copper powders upon sintering at 1120°C.

| Powders | Tensile-test bars | |
|-----------------------------|----------------------|-----------------------|
| | Length change [%] | Height change* [%] |
| Fe | -0.194±0.015 | -0.577±0.048 |
| Fe mixed with Cu (3 wt%) | 0.580±0.050 | 0.082±0.047 |
| Fe mixed with Cu (8 wt%) | 2.475±0.009 | 1.417±0.069 |

*The height of sample is parallel to the compaction direction

An interesting new result is that the compacts from coated powders shrank in the direction parallel to the compaction direction (the height of compacts) and swelled in the directions perpendicular to that (Table 2). But the amplitude of lateral expansion was much lower for coated-powder compacts than for comparable mixed-powder compacts.

Tab.2. Dimensional changes of compacts from copper-coated iron powders upon sintering at 1120°C.

| Starting powder mass | Tensile-test bars | | Cylinders | |
|------------------------------|-------------------|-------------------|---------------------|-------------------|
| | Length growth [%] | Height drop * [%] | Diameter growth [%] | Height drop * [%] |
| Fe coated with Cu (3 wt%) | 0.100±0.003 | -1.221±0.092 | 0.334±0.013 | -0.097±0.010 |
| Fe coated with Cu (8 wt%) | 1.275±0.015 | -0.543±0.337 | 1.188±0.082 | -0.004±0.059 |

*The height of sample is parallel to the compaction direction

WORKING HYPOTHESIS

The free energy of surfaces and interfaces becomes a dominant factor controlling the behaviour of coated-powder compacts immediately after the liquid phase forms. For the temperature considered, the specific energy of a free iron surface, γ_{Fe} , is about 1.9 J/m², the specific energy of a free surface of a copper melt, γ_{Cu} , is about 1.3 J/m², and the specific energy of the iron-copper interface, γ_{Fe-Cu} , is about 0.3-0.45 J/m² [1,8]. These represent approximate mean values, as the surface energy and its determination are very sensitive to the presence of small amounts of impurities, atmosphere, etc. But the important fact is that

$$\gamma_{Fe} > \gamma_{Cu} + \gamma_{Fe-Cu} \quad (1)$$

In such a situation, the thermodynamic imperative of reduction of the system's free energy enforces the copper-rich melt to spread out nearly uniformly on the largest possible surface area of solid iron particles. To do this, the melt also penetrates inter-particle contacts. So, the principal reason for dimensional changes of coated-powder compacts immediately after the liquid phase forms is the effort of the system to establish a more or less uniform covering of iron particles with a copper.

In the first approximation, the model of dimensional changes of coated-powder compacts consists of the following steps. Particles are initially coated with a copper layer of more or less uniform thickness. The uniformity of coating thickness is broken during compaction. When such a compact is heated above the copper melting point, copper melts and, driven by capillary forces, restores the uniformity of the coating thickness. This restoration of thickness uniformity causes the compact to swell. As the thickness of coatings was reduced primarily in lateral contacts and perhaps slightly also in axial contacts, the compact swells primarily laterally. Axial swelling is less expressive, Fig.3. Once the penetration of melt 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. The duration of heat determines the resultant dimensional changes upon sintering. Most powder metallurgy sintering is performed under conditions where the final part is shrunk axially and swelled laterally. If the compact is held at a peak temperature for a sufficiently long time, the compact will shrink both axially and laterally upon sintering.

The difference between axial and lateral contacts results from the character of powder motion. The movement of a powder mass undergoing uni-axial die compaction is believed not to be uniform across the die. Such an assumption is based on direct experimental results. Powder layers, which were parallel to each other and to the punch face at the beginning of compaction, were found bent in the direction of pressing after the uni-axial die compaction [9]. So, the powder mass moves more near the central axis and the axial movement decreases from the axis towards the die wall. That is, the nearer to the central axis the powder particle occurs, the greater axial displacement this particle undergoes during uni-axial pressing at ordinary pressures. This means that a particle moves (slides) axially with respect to its surroundings, Fig.4. The axial sliding leads to the wear of adjacent particle surfaces, that is to the damage and material loss from the inter-particle contacts parallel to the compaction direction [10].

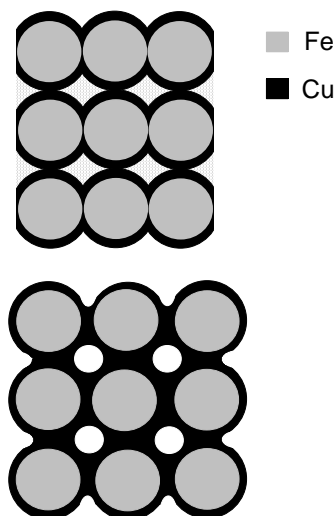


Fig.3. Schematic illustration of how the coated-powder compact swells. The molten copper restores the uniformity of coating thickness that was broken during compaction. The figure presents a state of compact before (the top part) and after (the bottom part) the liquid phase forms.

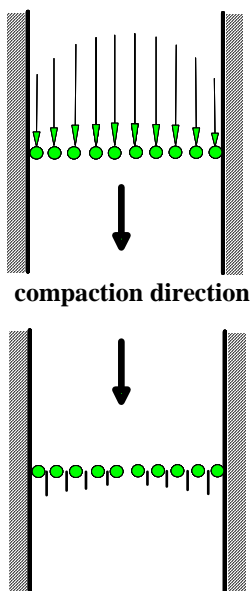


Fig.4. Schematic illustration of axial displacements that the particles of a typical layer of a green compact underwent during compaction (the top figure) and corresponding amplitudes of relative axial displacement of neighbouring particles against each other (the bottom figure).

Hence, the copper coatings can be thinned or removed from contacts parallel to the compaction direction during powder compaction. Wear debris and folds of a coating layer pushed out from the contacts are entrapped within inter-particle pores near these contacts. The coatings in contacts perpendicular to the compaction direction also deform by a plastic flow under normal indentation of core powder particles. But these deformations are considered negligible compared with deformations in lateral contacts and are not addressed in this contribution.

In accordance with the conceptions just presented, the maximum linear growth of compact results from the situation when (i) the copper coatings are as thick as possible, and (ii) they are entirely removed from relevant contact areas during compaction and then fully restored during sintering. The smaller the surface that a fixed amount of copper has to cover, the thicker the coating layer will be. A spherical particle has the minimum surface area for a given volume. Therefore, for the upper estimate of lateral swelling of a compact with a fixed copper concentration, particles are considered spherical. The relevant size of a green compact is then considered proportional to the diameter of a bare iron particle, d_{bare} , and the relevant size of a sintered compact is considered proportional to the diameter of a coated particle d_{coated} . The maximum relative linear swelling is then $(d_{coated}-d_{bare})/d_{bare}$. This leads to the relationship:

$$\left(\frac{\Delta L}{L}\right)_{\max} = \left(1 + \frac{c_{Cu}}{c_{Fe}} \frac{\rho_{Fe}}{\rho_{Cu}}\right)^{1/3} - 1 \quad (2a)$$

Here c_{Cu} , c_{Fe} and ρ_{Cu} , ρ_{Fe} are mass concentrations and mass densities of copper and iron, respectively. If the concentration of copper is low, the approximate relationship reads:

$$\left(\frac{\Delta L}{L}\right)_{\max} = \frac{1}{3} \frac{c_{Cu}}{c_{Fe}} \frac{\rho_{Fe}}{\rho_{Cu}} \quad (2b)$$

RESULTS AND DISCUSSION

As usual, compacts from a pure iron contracted in every direction and compacts from mixed iron and copper powders extended in every direction. Typical examples are presented in Table 1.

The dominant swelling mechanism accepted today for a mixed-powder compact is that a molten copper leaves its original sites and penetrates into contacts between iron particles. But for a compact from iron particles coated with copper, the copper layer is already sandwiched between iron particles. Therefore, an ordinary shrinkage of coated-powder compacts is expected.

But experiments show that the coated-powder compacts resemble neither pure- nor mixed-powder compacts in regards to the dimensional response. Compacts from a copper-coated iron powder usually contracted only along the compaction direction whereas they extended in directions perpendicular to that. Dimensional changes are analogous for both prismatic and cylindrical specimens. Typical examples are presented in Table 2.

A hypothesis on dimensional changes of coated-powder compacts is proposed in this article. The explanation is based on the premise that a molten copper restores the uniformity of coating thickness that was broken during compaction. The analysis based on this assumption provided the following estimation for a maximum linear growth:

$$\left(\frac{\Delta L}{L}\right)_{\max} = \left(1 + \frac{c_{Cu}}{c_{Fe}} \frac{\rho_{Fe}}{\rho_{Cu}}\right)^{1/3} - 1 \quad (3)$$

Consider the value of density of a bulk copper in this relation. The maximum linear growth of a compact containing 3 wt% of copper is then estimated as 0.9%, and that for a compact containing 8 wt% of copper as 2.5%.

The above described experiments carried out on compacts from iron powders coated with a copper provided the values of linear swelling from 0.1% to 0.4% for samples with 3 wt% of copper and from 0.41% to 1.48% for those with 8 wt%. The linear growth was higher for compacts containing 8 wt% of copper than for those containing 3 wt% of copper (Table 2).

Various properties of coated powders can affect the result. The thickness of a raw cemented copper layer can control the value of the wear coefficient. A thicker porous layer can be less wear resistant than a thinner one. Adhesion between the parent iron particle and a thick copper coating can be less than for a thin coating, etc. This increases the total removed volume of coatings with increasing copper content, which results in a higher swelling of the compacts after sintering.

CONCLUSIONS

Mixtures of iron and copper powders are widely used in a powder metallurgy. But the enormous expansion of compacts from such mixtures upon liquid phase sintering limits the use of this type of material for more precise parts.

The dominant swelling mechanism accepted today is that the copper is transferred from its original sites into the iron inter-particle contacts. The use of iron powders coated with copper is thus expected to restrain expansion as the copper layer is already present in the contacts. The goal of the investigation presented here was to check this assumption.

The results obtained can be summarised as follows.

1. Iron powder particles were coated with 3 and 8 wt% of copper through cementation. Bar-shaped and cylindrical samples were compressed at 600 MPa and sintered at 1120°C.
2. A surprising finding was that the samples shrank in the compaction direction and swelled in directions perpendicular to that.
3. To explain such anisotropy qualitatively, it was proposed that axial and lateral contacts between particles became unequal during powder compaction. The sliding of adjacent particles against each other degraded (wore) the copper coatings in contacts parallel to the compaction direction. This sliding resulted from the fact that the axial movement of compacted powder decreased from the central axis towards the die wall. A fraction of copper was transferred from contact regions into near inter-particle pores. When the compact was heated above the copper melting point, copper melted and restored the nearly uniform covering of iron particles. As a result, lateral swelling of the compact arose. Once the penetration of melt was complete, more gradual densification process took place. This reduced sample axial dimension and also offset a part of lateral swelling.
4. To quantify the lateral swelling, a rough quantitative estimate based on the above qualitative considerations was proposed.

An estimate obtained for the maximum linear swelling is very rough. A more consistent theory is desirable that will relate the lateral growth of compact to the amount of worn material. And a model is required that will connect the wear of coatings with more

convenient quantities, such as internal friction and cohesion of powder mass, friction between powder mass and die wall, characteristics of applied load, etc. This improvement in theory and more comprehensive experiments (with powders coated under different conditions, through various methods (e.g. electroplating [11,12]), etc.) represent the objectives the further investigation.

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REFERENCES

- [1] Kaysser, WA., Huppmann, WJ., Petzow, G.: Powder Metallurgy, vol. 23, 1980, p. 86
- [2] Wanibe, Y., Yokohama, H., Itoh, T.: Powder Metallurgy, vol. 33, 1990, p. 65
- [3] Dubief, D., Hodaj, F., Allibert, CH., Rezel, D. In: Proceedings of Powder Metallurgy World Congress, Kyoto, 12-16 november 2000, p. 643
- [4] Zhang, Z., Sandström, R., Wang, L.: Journal of Materials Processing Technology, vol. 152, 2004, p. 131
- [5] Radchenko, OG., Getman, OI.: International Journal of Hydrogen Energy, vol. 26, 2001, p. 489
- [6] Danninger, H., Strobl, S., Gärtenhofer, R. In: Proceedings of the 1998 PM World Congress, Granada 1998, Vol. 1, p. 185
- [7] Strobl, S., Gierl, C., Konnegger, T., Kupková, M., Kabátová, M.: Powder Metall. Progress, vol. 6, 2006, p. 149
- [8] Matsumoto, T., Fujii, H., Ueda, T., Kamai, M., Nogi, K.: Meas.Sci.Technol., vol. 16, 2005, p. 432
- [9] Krezalek, IC., Sivakumar, K.: Journal of Materials Processing Technology, vol. 48, 1995, p. 421
- [10] Meng, HC., Ludema, KC.: Wear, vol. 181-183, 1995, p. 443
- [11] Oriňáková, R.: Surface & Coatings Technology, vol. 162, 2003, p. 54
- [12] Oriňáková, R., Turoňová, A., Kladeková, D., Gálová, M., Smith, RM.: Journal of Applied Electrochemistry, vol. 36, 2006, p. 957