

# SLS Application of the Fe-Cu-C System for Liquid Phase Sintering

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## Abstract

The present work suggests the possibility to exploit the phenomena of copper swelling, and the controlling effect of carbon during liquid phase sintering, to be used in SLS technology to achieve temperable tooling materials in a single furnace cycle. As a basic investigation of this possibility, four powder samples of different copper and carbon content were tried and evaluated in respect to SLS and furnace behavior. The possibility to form green bodies was verified and the different sintering behaviors were studied. It was concluded that this material system holds several interesting phenomena that, if properly managed and if sufficient fractional packing density could be reached, could open distinct possibilities to achieve high quality material for SLS tooling purposes.

## 1. Introduction

Over the last decade, the field of Solid Free form Fabrication (SFF) has seen the development of several new tooling techniques. Among the more widely used are the SLS based systems: the Sinterstation from DTM-Corp, Austin TX, and the EOSINT-M from EOS GmbH, Munich, FRG. Both systems have the capacity to build in iron-base metal, but where the Sinterstation is a multi-material system with an indirect approach to metals, the EOSINT-M is specialized on metals with a direct approach. The indirect approach means that the material has to go through further processing to achieve satisfactory properties, for example: DTM's RapidSteel 2.0 material requires, apart from SLS processing, two subsequent furnace cycles for the sintering and infiltration to full density. This is time consuming, and the infiltration by a second component limits the achievable material properties. The direct approach of EOS means that the metal material is actually sintered by the laser, but by doing so, the material is subjected to pointwise heating and cooling, with the stress that follows. This approach limits the choice of suitable material systems, and thus also limits the achievable material properties. Both approaches give a surface equivalent to the fineness of the powder, and none of the commercially available material systems is hardenable.

This implies that there could be use for a material system with more production-tool-like properties. Due to the inherent stress, the direct SLS approach is less suitable for the processing of a hardenable material. In the indirect approach, on the other hand, such a material system is more feasible, but would require that a satisfactory density could be achieved without infiltration, preferably in a single furnace cycle.

## 2. Hypothesis and theoretical background

It is the hypothesis of this paper that there is a distinct possibility to exploit the characteristics of liquid phase sintering within the Fe-Cu-C system to achieve a material that allows the SLS based manufacturing of satisfactory tools, with the capacity for heat-treatment to further control material properties.

### 2.1 Liquid Phase Sintering

Liquid phase sintering is one of the most popular methods to enhance the sintering behavior of a powder material. During liquid phase sintering, a liquid phase coexists with a particulate solid at sintering temperature [1]. If the liquid's wetting properties of the solid particulate are good and the material of the solid is soluble in the liquid phase, there will be an enhanced sintering over all wetted surfaces. This enhanced sintering implies growth along the wetted grain boundaries. Grains situated at a free surface will thus expand in all lateral directions, whereas the un-wetted free surface is depleted of material. This can lead to a smoothing effect on the material surface [2]. For the most part, in conventional powder metallurgy, liquid phase sintering exhibits sufficient internal force through liquid capillary action on the particulate solid that external forces are not required for the compaction during sintering [1].

### 2.2 The Fe-Cu-C system

Copper as an alloying substance has unique properties in the field of sintered steels. Copper in small amounts does not only improve strength and rust resistance, it also melts at a lower temperature, has a rapid surface diffusion over solid iron, and a liquid phase where iron easily diffuses [3]. This has made copper a popular choice as the liquid phase, in liquid phase sintering of iron base alloys. However, copper is rapidly dissolved into the steel particles (up to approximately 8.5%), forming a substitutional solid solution. Since copper atoms have a larger diameter compared to iron atoms, this causes a distortion in the crystal structure and thus resulting in a swelling effect, that is larger than the original copper volume [3][1].

Furthermore, the addition of carbon lowers the liquid temperature of the Cu-Fe melt, and delays the dissolution of copper into the steel thus allowing a prolonged time with liquid phase sintering. Fortunately, the suitable copper and carbon levels fall within the span of improved strength and toughness, as well as temperable properties [3] of the steel. These phenomena are well known in conventional powder metallurgy, and by the correct composition within this material system it has been possible to manufacture powder grades with zero dimensional change during sintering to full density.

### 2.3 SLS Aspects

Apart from having excellent sintering and densification properties during the furnace cycle, a practical powder blend for indirect SLS application is required to process well in the

SLS equipment to yield satisfactory green bodies. This means that there must be an efficient binder system, and, in the interest of high precision and high density, it is desirable to use a powder blend with the highest possible fractional packing density.

The fractional packing density of a free flowing powder is primarily dependent on grain size distribution, the proportions, and the mixing of the powder. The density of SLS manufactured objects would be especially dependent of the arrangement (i.e. the mixing) of particles with different sizes in each new layer. This has been investigated in [5], where a substantial increase was achieved for a two-component system using a Doctor's blade [5] and in [8], where the counter-rotating roller, such as used in the Sinterstation system, was associated with frictional shear in the underlying layers, [8]. However the roller's transport of the powder, in a wavelike motion, is very similar to the cascading motion that, in a horizontal rotary blender, generally is associated with optimum blending conditions [6]. Assuming that the powder mass is well mixed in the powder containers, it could probably be assumed that a well designed, multi-component powder blend would yield a substantially higher fractional packing density when applied into a SLS system.

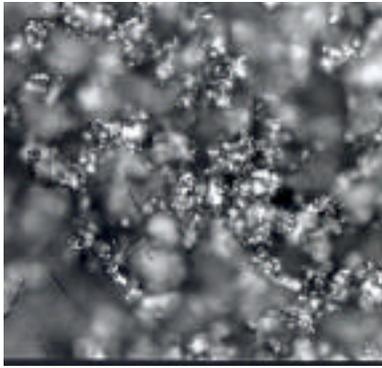
The addition of binder could either be in the form of powder mixed with the metal powder, or as coated on the particulate [7]. Coating is associated with higher green strength but, since the binder is removed during the furnace cycle, is more sensitive to the thickness of the binder layer. For experimental use, it is however easier to add the binder in the shape of a powder.

### 3. Experimental

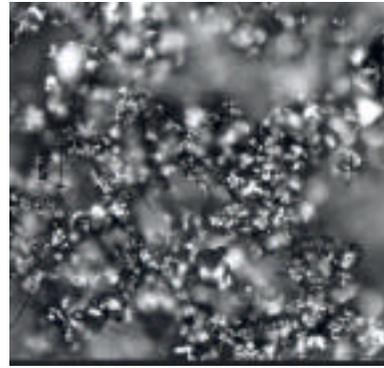
The experiments are intended to investigate a) how a Fe-Cu-C commercially available powder system would process under "normal" SLS conditions, and b) how the sintering behavior is influenced by the presence of copper and carbon in the powder blend.

#### 3.1 The powders

For this purpose, two different powder grades from Höganäs AB were selected; Distaloy Acu, with 10% Cu added, and Distaloy DH-1 with 2% Cu added. To ensure even copper distribution, this family of powder grades, has the copper diffusion bonded to the surface of the steel grains. The materials in both these grades are temperable.



*Fig.1. Powder grains; Distaloy ACu*



*Fig.2. Powder grains; Distaloy DH-1*

The powders were sifted to a maximum grain size of 63  $\mu\text{m}$ . Given the uncontrolled grain size distribution and the coarse structure of the individual grains (*Fig. 1 & 2*), these powder samples had very low apparent densities; Distaloy ACu: 3.97  $\text{g}/\text{cm}^3$  ? 49.9% of theoretical density and Distaloy DH-1: 3.66  $\text{g}/\text{cm}^3$  ? 46.4% of theoretical density. This will be inherited as a low fractional packing density in the green bodies, but will facilitate the observation of changes in the powder structure during sintering. However it also means that we despite substantial shrinkage hardly can expect to achieve full density at this stage.

For the binder system, a 5 % addition of Hexamethylene Tetramine Phenol was used. Being a phenol based binder it could be expected to function under similar conditions as the binder system in RapidSteel 2.0. As mentioned previously, for this experimental case, the addition of binder by the mixing of powder was found more practical. Two samples of each powder grade, ACu and DH-1, were mixed with binder, and as a source of carbon, 1% graphite powder was added to one sample of each grade, samples ACu+C and DH-1+C.

### 3.2 SLS processing

The four sample blends were SLS processed with identical build files under conditions similar to the standard settings for RapidSteel 2.0.

### 3.3 Furnace processing

The samples were sintered together in a graphite crucible, in a vacuum furnace, according to the following cycle: 20 – 600 °C, (the binder burnout stage), raise 150 °C/h. At 600°C, raise temperature in a single step to 1120 °C, (the sintering stage), and remain for two hours. Then let the furnace cool at its own pace.

## 4. Results and discussion

The selected powder fractions of both grades spread and leveled well as layers in the Sinterstation. The laser scanning was accompanied by some spectacular sparkling and smoking, but green bodies were formed, however weak and with a very low fractional powder

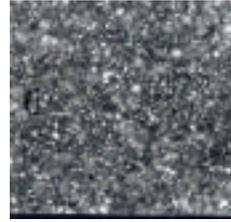
packing as was predicted, but still quite possible to handle. Powder packing in the green bodies as well as grain shapes can be seen in *Fig. 3,4,5, & 6.*



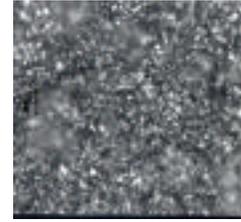
**Fig.3** Distribution and packing of powder in a green body of sample ACu.



**Fig.4** Distribution and packing of powder in a green body of sample ACu+C.



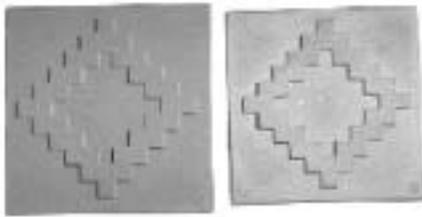
**Fig.5** Distribution and packing of powder in a green body of sample DH-1



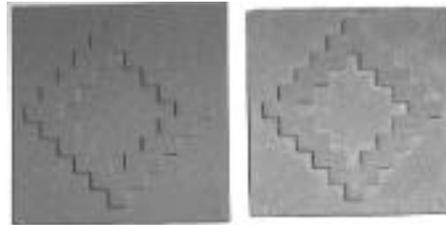
**Fig.6** Distribution and packing of powder in a green body of sample DH-1+C.

#### 4.1 Shrinkage

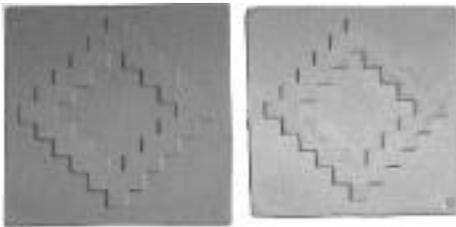
After furnace processing the samples have sintered and show a substantial shrinkage, *Fig. 7, 8 and 9, 10.* Since the green bodies, and apparently also the sintered products have a considerable porosity, an absolute quantitative study of the shrinkage would not only be inconclusive, but also possibly misleading. A qualitative comparison, on the other hand, could give an indication of the influence of copper as well as carbon. Shrinkage factors can be seen in Table 1.



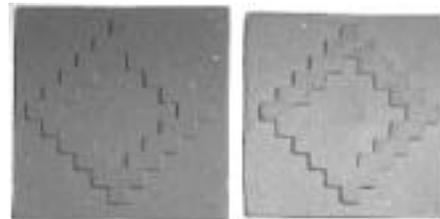
**Fig. 7.** Green body and sintered sample: ACu.



**Fig.8.** Green body and sintered sample: ACu+C.



**Fig.9.** Green body and sintered sample: DH-1.



**Fig.10.** Green body and sintered sample: DH-1+C

**Table 1.** The shrinkage in different directions during sintering of green bodies of the chosen powder grades and blends.

Shrinkage	ACu	Acu+C	DH-1	DH-1+C
X	6.70%	4.97%	3.99%	3.00%
Y	6.41%	4.97%	3.84%	3.14%
Z	3.22%	3.17%	1.59%	1.61%

In general we find that the copper rich ACu powders show a larger shrinkage in all directions, compared to the DH-1 powders. This may seem to contradict the thesis on copper swelling, however there are two points to consider: First, the calculated shrinkage factors do not take any account to the porosity, thus there is no information of possible swelling in the base material. Second, liquid phase sintering continues as long as there is a liquid phase present. In the DH-1 powder samples, all the copper (2%) is dissolved into the steel, whereas the copper content of the ACu powders (10%) is higher than coppers solubility at sintering temperatures (approx. 8.5%), thereby the liquid phase sintering, and the related shrinkage, of ACu powder samples continues until the temperature drops below the melting point of copper.

The shrinkage of the carbon-enriched samples is considerably smaller than the carbon free samples. This may also seem like a contradiction of the thesis of prolonged liquid phase sintering, but again, no conclusions can be drawn until porosity has been taken into account. Some differences in shrinkage between x-, y- and z –directions could possibly be accounted for by machine and process variables, it is however notable that the shrinkage in z-direction is almost half the shrinkage in x- or y-direction. This could indicate that the powder in each layer may have been closer packed in z-direction.

Apart from these points, the shrinkage seems almost surprisingly linear considering the low packing density in the green bodies. The magnitude of this shrinkage demonstrates the power of the densifying effect of liquid phase sintering in the Fe-Cu-C system.

#### 4.2 Copper-swelling

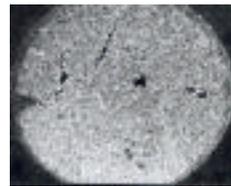
The effect of the copper-swelling phenomenon can be estimated by the comparison between the macro magnifications of the ACu samples and DH-1 samples, **Fig. 11, 12 and 13, 14**. In the DH-1 samples, the shrinkage and rearrangement has been so severe that gigantic pores have formed in a crack like manner. In the ACu samples there are no such “super-pores”, apparently the copper-swelling effect has compensated for the most dramatic changes.



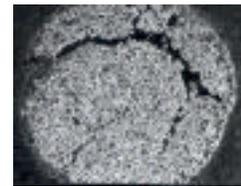
**Fig.11.** Macro-structure of the sintered sample ACu. Coarse, sponge-like structure with almost uniform porosity.



**Fig.12.** Macro-structure of the sintered sample ACu+C. Finer sponge-like structure with almost uniform porosity.



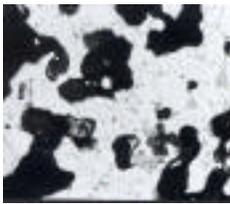
**Fig.13.** Macro-structure of the sintered sample DH-1. Finer sponge-like structure where shrinkage and rearrangement is evident.



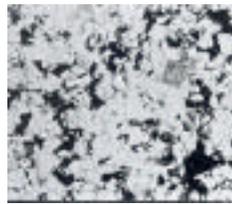
**Fig.14.** Macro-structure of the sintered sample DH-1+C. Coarse sponge-like structure where shrinkage and rearrangement is evident

The effect of carbon presence can be illustrated by comparison between the different DH-1 samples **Fig. 13** and **Fig.14**. Sample DH-1+C has obviously experienced the longer period with liquid phase sintering, resulting in fewer, but larger pores, coarser sponge-like structure and smaller grain surface area compared to sample DH-1.

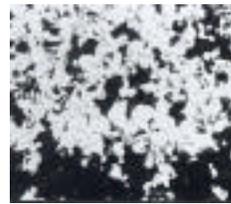
A similar comparison between the ACu samples reveals a more complex situation, **Fig.11** and **Fig.12**. In this case the carbon added sample has the finer structure. This could however be explained by the fact that ACu powder carries an excess of copper and thus all copper can not be dissolved into the steel, which, in turn, means that liquid phase sintering continues in both samples as long as the temperature allows it. However this does not explain why the structure in sample ACu+C is finer than sample DH-1+C, and apparently has been less affected by liquid phase sintering. This indicates even more complex and dynamic phenomena, but could possibly be explained by the following hypothesis: The higher the concentration of carbon in a Fe-Cu-C melt the steeper the wetting angle, and thus the poorer wetting properties on an iron based alloy. Poorer wetting properties mean smaller amount of copper in direct contact with base material and thus delayed penetration of copper along the grain boundaries. This accounts for the prolonged presence of a liquid copper phase, whereas the decreased wetting properties explain why the ACu sample had sintered further than the ACu+C sample. Since the carbon present dissolves into the liquid phase and ACu powders carry 10% copper, whereas DH-1 powders carry only 2%, there will be a much lower concentration of carbon in the liquid phase of the ACu+C sample. That makes the copper more inclined to dissolve the base material thus causing a swelling, which of course also expands the grains' surfaces. The carbon concentrated liquid phase of the DH-1+C sample is less inclined to release copper, and thus the liquid phase sintering will continue to decrease the free grain surfaces, thereby concentrating the liquid phase over a smaller area, which in turn increases the effect of liquid phase sintering. On the other hand, when the copper dissolution in sample ACu+C has concentrated the carbon present in the liquid phase to the same level as in sample DH-1+C, the liquid phase with its decreased wetting capacity, has been spread over a much larger area and thus diminished the effect of liquid phase sintering.



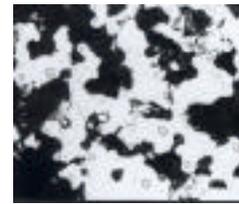
**Fig.15.** Sintered micro-structure of sample ACu. Large, but comparably smooth pores, with a higher fraction metal compared to sample DH-1.



**Fig.16.** Sintered micro-structure of sample ACu+C. Smaller, but comparably coarse pores, with a higher fraction metal compared to sample DH-1+C.



**Fig.17.** Sintered micro-structure of sample DH-1. Higher porosity and smaller, much coarser pores compared to sample ACu.



**Fig.17.** Sintered micro-structure of sample DH-1+C. Higher porosity but larger smoother pores compared to sample ACu+C.

Figures *15, 16* and *17, 18* further illustrate the above-mentioned phenomena. However comparison between the shape of different sponge structures and the powder shape and distribution in the green bodies, *Fig. 3, 4* and *5, 6*, demonstrates that the surfaces of the solid indeed have become smoother, even if the smoothness is on a very small scale in these porous samples.

## 5. Conclusions and further work

It has been established that the Fe-Cu-C system can be processed in SLS equipment, forming green bodies, with the capacity for furnace processing. It has also been found that the Fe-Cu-C system contains several interesting and complex phenomena that if properly managed could be useful in SLS application. Among those are: liquid phase sintering with enhanced sintering behavior, densification, some smoothing effect on free surfaces, and copper swelling that could compensate for some shrinkage. The liquid phase was found to interact with the concentrations of copper and carbon, thus the rate of sintering and sintering behavior can be further controlled. But the possibility to exploit these properties for SLS purposes is dependent on whether green bodies of sufficient fractional packing density can be manufactured, which in turn is dependent on the composition of the free flowing powder and the achievable density during the spreading of each new powder layer. This is obviously an area where considerably more work must be applied.

## References

1. German R.M. "Liquid Phase Sintering" Plenum Press 1985.
2. Park, H, et al., "An analysis of the Surface Menisci in a Mixture of Liquid and deformable Grains" Metallurgical Transactions, vol. 17A, Feb. 1986, pp 325-330.
3. Runfors, U. "Powder metallurgy", Dep, of Physical Metallurgy, KTH, Sweden 1987. (In Swedish)
4. German R.M. " Powder Metallurgy Science", MPIF 1994.
5. Karapatis, N, et al. "Optimization of Powder Layer Density in Selective Laser Sintering" Bourell, D.L.,et al., editors, Proceedings of the Solid Freeform Fabrication Symposium 1999, The University of Texas at Austin 1999, pp 255-263.
6. Parent, J.O.G., et al., "Fundamentals of Dry Powder Blending for Metal Matrix Composites", The International Journal of Powder Metallurgy, vol.29, No.4, American Powder Metallurgy Institute, 1993.
7. Beaman, J.J., et al. "Solid Freeform Fabrication: A New Direction in Manufacturing", Kluwer Academic Publishers, 1997.

8. Van der Schueren, B. & Kruth, J.-P. "Powder deposition in selective metal powder sintering", Rapid Prototyping Journal, vol.1, No.3,1995 pp.23-31.