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A new densification mechanism of copper powder sintered under an electrical field

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A new sintering mechanism is revealed for copper powder sintered under the influence of an electrical field and a force field during the formation of microcomponents. Analysis of the microstructure and grain boundary evolution of the sintered samples showed that the disappearance of the interface at contact areas between particles is a continuous process which involves new grain formation and grain refinement during this innovative microsintering process. The densification process is therefore different from what is known in a conventional powder sintering process.
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Over the last two decades, the development towards miniaturization of products and devices in industries such as electronics, optics and communications has increased the demand for metallic parts manufactured at the microscale. During the last 10 years, various micrometal-forming processes have been studied and used to produce a variety of micrometal components. In particular, such processes have been studied as part of the EU large-scale integrated project MASMICRO, which researched and produced various manufacturing facilities for micromanufacturing [1].

The use of microcomponents as well as intensive competition on manufacturing cost led to the requirement for cost-effective production of these components without much compromise on their final quality. To address this issue, a novel microforming technology, named Micro-FAST (combining microforming and field-activated sintering technology (FAST)), was proposed recently by the present authors for the forming of microcomponents [2–5]: the process is illustrated in Figure 1. Micro-FAST is a method which can be used for the forming of microcomponents with a variety of material systems, e.g. copper gears (shown in the bottom right corner of Fig. 1), have been fabricated successfully at the microscale. Over the last few years, pioneering work has been carried out by several authors and many interesting experimental results have been achieved. First, Micro-FAST is an efficient process: the entire forming process can be accomplished within a few seconds, and the relative densities of the formed microcomponents are high. Furthermore, of the sintering parameters, the heating rate, sintering temperature and heating cycle all have a significant effect on the densification of the metal powders during the sintering process [2,5]. Moreover, with continuous high pressures being applied and the short forming time, Micro-FAST occurs without coarsening of grains during the densification process [4]. Joule heating is the main heat source during the sintering process, and thus the process has different densification mechanisms compared to those of conventional processes (including FAST or spark plasma sintering (SPS)). Lastly, the densification mechanism of metal powder is related to plastic deformation and the interfacial melting of particles. A three-stage sintering model has been established to describe the process of the densification of 316L stainless steel powders when being sintered by Micro-FAST [3]. For the densification process in a traditional powder sintering method, grain growth and neck growth are the two critical mechanisms to achieve densification. Grain growth is caused by coarsening, which is associated with either surface diffusion or evaporation/condensation [6]. Grain coarsening can also be observed in other FAST methods [7,8]. However, the mechanisms of neck formation during the sintering of metal powder without grain growth for enhanced densification in Micro-FAST are virtually unexplored.

The purpose of the present work was to study the mechanism of copper powder densification at the microscale in a Micro-FAST process, based on scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analysis. This kind of work has not been done by other researchers. The main objectives were to establish the geometric model of grain

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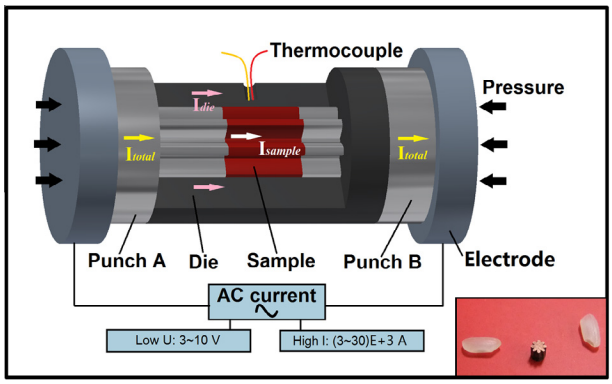


Figure 1. Illustration of the Micro-FAST sintering and forming process.

evolution between the two particle contact areas during this innovative microforming process. The new understanding developed would help to develop a new processing strategy for this kind of powder, as well as providing better quality control during the sintering of microcomponents.

Commercially pure copper powder (99.7% purity, 0.05 wt.% Pb, 0.05 wt.% As, 0.05 wt.% Fe, 0.05 wt.% Sb), with an average particle size of 20 μm, was used for the experiment. The powder was purchased from CNPC Powder (Shanghai, China). A scanning electron micrograph of the initial powder is shown in Figure 2(a). The atomized powder also contain a fraction of fine particles of size <10 μm.

A stepwise experiment was designed to study the grain evolution and the process being carried out in a vacuum ($<10^{-4}$ Pa). In the Micro-FAST process, the as-received powder consisted of agglomerates which were suitable for making up a microgear with a pitch diameter of 1.6 mm. After weighing, the loose powder was loaded into a die. The die was then placed into a Gleeble-1500D machine, and heated rapidly to a particular sintering temperature at a preset heating rate (a high electric current passes through the die set). At the same time, a preset pressure was applied to the punch. The detailed technological parameters of the experiments are given in Table 1.

After sintering, the microstructure of the samples was observed under a JSM-5900LV scanning electron microscope (JEOL, Japan), and TEM and HRTEM observations were performed using a JEOL JEM-2010F microscope operating at 200 kV.

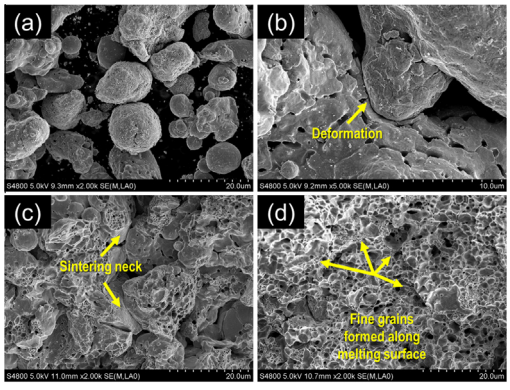


Figure 2. SEM micrographs of the fracture surface of the samples: (a) the initial copper powder; (b) 1#, sintering at 200 °C; (c) 2#, sintering at 600 °C; (d) 3#, sintering at 600 °C with five heating cycles.

The SEM micrographs of the fracture surface of the samples sintered at different levels are shown in Figure 2. Comparing the micrographs in Figure 2, it can be seen that, at different sintering levels, the contact state between particles developed from "point contact" to "lineal contact" and then "surface contact". Lu et al. [2] have reported that if the temperatures at the contact areas between particles are high, the yield stresses of the material at the contact areas and the viscosity of the compact will decrease. Therefore, the deformation rate of the material at a contact area will be greater when the temperature is high. Similarly, the distances between particles will decrease under high pressure and the contact areas will become larger. The microsized pores within the powder compact will be filled with neighboring powder particles due to bulk and plastic flow. This is largely due to the effect of electroplasticity [9]: it was found that an electric field of ~1 kV cm^{-1} could significantly reduce the plastic and fracture stresses of metals at room temperature. It was subsequently confirmed that the electric field also lowered the brittle-to-ductile transition temperature, reduced the flow stress and increased the elongation at elevated temperatures.

A further important observation is that the formed microgear had good mechanical properties. As shown in Figure 2(c) and (d), the fractography of the fracture section was typically of a dimpled nature, which indicates that the fracture belongs to ductile fracture, with enlarged dimples and more liquid phase formed [10]. The welded joints between particles observed in Figure 2(c) are clear evidence of the formation of the liquid phase. This figure also shows that, provided that a significant amount of heat is generated at the interface of the particles, the melting point of fine powder particles is likely to be achieved at those interfaces that cause the generation of a liquid phase at local areas. Once the liquid phase is formed, it will lead to the melting of the contact surface between particles [11]. At the same time, with the aid of the pressure applied to the compact, the liquid phase flows into the vicinal pores due to viscous flow and capillary force [12], which results in the disappearance of the interface between particles and fast densification of the compact (see Fig. 2(d)).

Moreover, upon investigation of the sizes of grains inside the particle, it is interesting to note that no coarsening of grains accompanied the process of the densification of the microsized compact. However, as shown in Figure 2(d), when the formed microparts have nearly obtain full relative density (99.23%), a quantity of fine grains is formed along the particles' edge, especially at the interface melting areas between particles.

The ABEQUS FE code was used for an electrical-heat analysis. A simulated current density distribution in the two assumed copper powders during the sintering is shown in Figure 3(a). It can be seen that there was an electric current concentration in the neck area of the sintering. This could be a main cause of the particles' deformation to an equilibrium size, and the melting of interfaces occurred at this area. This is also evident in the sample shown in Figure 3(b), where formation of the liquid phase and fine grains between two particles are clearly seen. Furthermore, twin boundary migration (as shown in Fig. 3(c)) is observed, and this can become a significant electroplasticity mode. This investigation strongly suggests that the twin grain growth plays a deterministic role in the structural refinement [13].

We conclude from these observations that the applied AC field (low voltage: 3–10 V; high electric current: 3–30 × 10^3 A) leads to welding of the powders/grains that are in contact within a very short time (a few seconds) in

Table 1. The processing parameters corresponding to the samples formed.

Specimen designation	Heating rate (°C s^{-1})	Pressure on the punch (MPa)	Sintering temperature (°C)	Heating cycle number* (*T*–300 °C)	Total using time (s)	Relative density (%)
1#	50	75	200	0	48	73.46
2#	50	75	600	0	76	91.27
3#	50	75	600	5	148	99.23

* A heating cycle is defined as a cycle during which the temperature rises to the maximum value and then drops to about 300 °C.

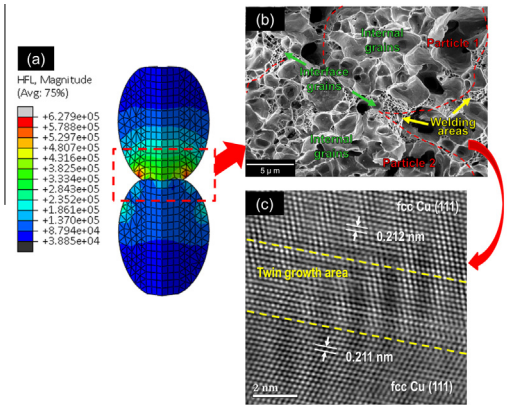


Figure 3. (a) Simulated current density distribution in the two assumed copper powders; (b) SEM micrograph of the fracture surface; and (c) HRTEM image of a copper particle in the formed 3# sample sintered at 600 °C with five heating cycles.

such a fast sintering process as Micro-FAST. The strong "particles' contact melting" structure is, in some aspects, very similar to certain grain welding structures [14,15].

However, in SPS, as the pulse is very short (~2 s) and the heat generated is not enough to really affect sintering, a further dwell sintering time (>5 min) appears to be necessary on account of the presence of the neck generated by volume diffusion [16]. The same mechanism, also reported in FAST [17] and electric-current-assisted/activated sintering [18], promotes densification by the simultaneous action of a high direct current through graphite dies and uniaxial pressure.

Attempting to obtain a strong neck connect between two particles, the microstructural studies focused on interface grains in the "welding areas". As shown in Figure 3(b), there were a number of fine grains formed along the edge of particles 1 and 2, and especially in the interface melting areas between the two particles. Grain refinement is one of the most important means of improving an alloy's mechanical properties and there are many means to refine the grain, including increasing the cooling rate in the alloy solidification process and mechanical–physical refinement [19]. In fact, these two methods were involved in the Micro-FAST sintering process. However, according to the fracture surface in Figures 2 and 3, the fracture plane, i.e. the hardness reduction, usually happens in the "welding areas", even though the grain size in such areas is remarkably smaller than that of the internal grains. In a study of copper joints this phenomenon was believed to be a result of the annealing effect exerting a larger effect than grain refinement on the mechanical properties [20]. Another important reason for the hardness reduction of the "welding areas" is the residual porosities formed among the "welding areas" (see Fig. 3(c)). During the tensile test, because the stress concentrates around the porosities, the microcrakes usually initiate from these weakest positions, then propagate to fracture the joints.

Figure 4 shows TEM images of the microstructure of the "welding areas" obtained at different sintering levels, as well as the model of different stages of grain boundary evolution during Micro-FAST.

First, a contact between grains [21] occurs through the mating surfaces (see Fig. 4(a)).

During the second stage (see Fig. 4(b)), some new grains are formed at the grain boundaries [22]. It is more interesting to note that the new grains are formed at a low temperature (200 °C), In fact, the temperature (200 °C) was tested near the sample's surface, and the local temperature is greater due to the local field intensification at inter-particle contact areas. However, the total heating time is only a few seconds, which results in the incomplete formation of new grains (indicated by the arrow in Fig. 4(b)).

During the third stage (see Fig. 4(c)), diffusion within grain boundaries predominates, thus diminishing pores and ensuring the arrangement of grain boundaries. However, the diffusion of grain boundaries is still not complete, because of the short sintering time and the high cooling rate (20 °C s^{-1}). Fang et al. [23] reported that the diffusion ability of the copper atoms decreases as the temperature drops and the atoms almost stop moving at the temperature of 600 K. This indicates that the system has transformed from the supercooled liquid state. In fact, the microstructure of the metal changes in several ways during the deformation process at high temperature. First, and most obviously, the grains change their shape and there is a surprisingly large increase in the total grain boundary area. A new grain boundary area (see Fig. 4(b)) has to be created during deformation, and this is done by the incorporation of some of the dislocations (see Figs. 3 and 4(c) and (a)) that are continuously created during the deformation process. A second obvious feature, recrystallization, involved the formation of new strain-free grains in certain parts of the specimen (see Fig. 4(b)) and the subsequent growth of these to consume the deformed or covered microstructure (see Fig. 4(c)). The unqualified term "recrystallization" always used to mean the primary recrystallization of the deformed microstructure. It is convenient to divide primary recrystallization into two regimes: nucleation, which corresponds to the first appearance of new grains in the microstructure; and growth, during which the new grains replace deformed material. Although these two events occur consecutively for any particular grain, both nucleation and growth occur during the sintering process in Micro-FAST. The kinetics of recrystallization is therefore superficially similar to that of a phase transformation which occurs by nucleation and growth [24].

During the last stage (see Fig. 4(d)), grain refinement dominates and the sintering process is completed, while nanosized residual pores are still distributed at the grain boundary. From the microstructure characterization shown in Figure 4(d), a twin structure (indicated by the arrow in Fig. 4(d)) is formed after sintering at 600 °C with five heating cycles. Although nanosized twins can lead to a significant increase in flow stress of ultrafine-grained pure copper [25], in the present study the width of the twin lamellae formed in the "welding areas" is about several hundred

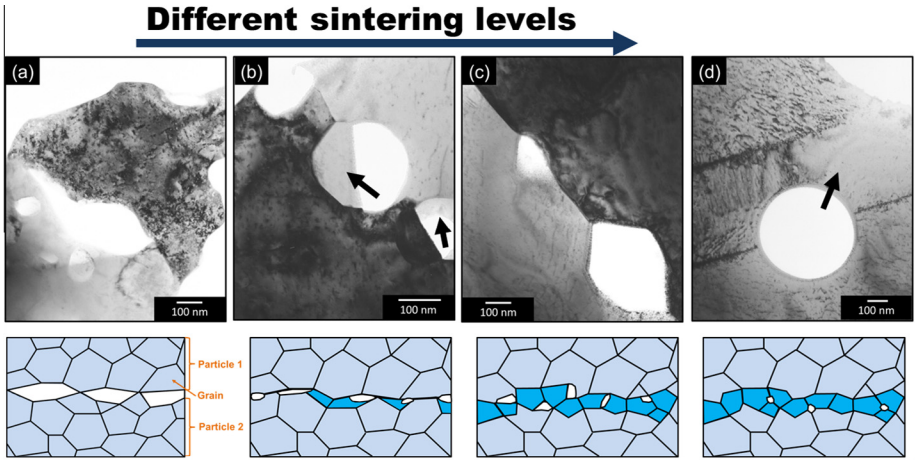


Figure 4. TEM images and model of different stages of grain boundary evolution during Micro-FAST: (a, b) 1#, sintering at 200 °C; (c) 2#, sintering at 600 °C; (d) 3#, sintering at 600 °C with five heating cycles.

nanometers, which is slightly too small and so that cannot obviously improve the mechanical properties. Furthermore, a dislocation-free area usually forms close to the twin structure, and this will inevitably decrease the yield strength of the original hardened materials. Moreover, the presence of porosity in the grain boundary is one of the major concerns with a powder sintering process, even for the mature powder metallurgy method. The high porosity is also one of the most important factors in the reduction of the failure strength of "welding areas". Because of the large freezing temperature range, there is large solidification shrinkage and a high coefficient of linear expansion, after which any blanks in the expanded space become pores [26].

Nevertheless, the hardness of the "welding areas" can be improved by increasing the applied load due to the formation of a high density of dislocation cells and microstructural refinement [27]. That is to say, using a slightly higher sintering temperature can increase the quality of the liquid phase formed between two particles. At the same time, increasing the amount of pressure applied to the punch slightly can produce more dislocations, which will help the liquid phase to complete refinement during the cooling process.

In summary, the whole densification process of copper powders in Micro-FAST can be completed within a short time due to the densification process being a continuous process which involves plastic deformation and the interfacial melting of particles. Under the effect of coupled multi-physical-fields, when the particles are deformed to an equilibrium size, the grains at the contact areas between two particles can be welded in a few seconds in this fast sintering process. Moreover, new grains can be formed, and grain refinement will occur during this fast grain-joining process, which will lead to the disappearance of the interface between two particles. The densification process is therefore remarkably different from that in a conventional powder sintering process.

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