ELSEVIER

Powder metallurgically manufactured cellular metals from carat gold alloys for decorative applications

SPECIAL FEATURE

Olaf Andersen[a,*], Hartmut Göhler[a], Cris Kostmann[a], Peter Quadbeck[a], Frédéric Diologent[b], Damien Colas[b] and Bernd Kieback[c]

[a] Fraunhofer IFAM, Branch Lab Dresden, Winterbergstr. 28, 01277 Dresden, Germany
[b] Varinor SA, Rue St-Georges 7, CH-2800 Delémont, Switzerland
[c] Technical University of Dresden, Institut für Werkstoffwissenschaft, Helmholtzstr. 7, 01067 Dresden, Germany

This paper explores the possibilities of producing visually attractive cellular gold structures via two different powder metallurgical approaches: sintering of loosely packed gold fibers and replication of polymeric templates. In the latter case, two different templates were used: reticulated polyurethane (PU) foam and expanded polystyrene (EPS) spheres which were coated with atomized gold powder. In contrast to the fiber route, replication techniques require an intermediate thermal treatment for the removal of the templates prior to sintering. Typical carat gold alloys lend themselves for supersolidus liquid phase sintering due to a sufficient difference between solidus and liquidus temperature. This approach was applied to all three manufacturing routes and rigid cellular gold structures were obtained successfully in all cases.

Powder metallurgical manufacturing routes for cellular metals

Two different approaches were explored for obtaining highly porous cellular gold structures:

- Sintering of gold fibers;
- Replication of polymeric templates in the form of polyurethane (PU) sponges and expanded polystyrene (EPS) spheres.

The fiber structures and the replicated sponges were made from 18 ct. alloys while the hollow spheres were produced from a 14 ct. alloy. The basic processing steps of all routes are shown in Fig. 1.

In order to obtain suitable fibers, the crucible melt extraction (CME) process was chosen which allows for the manufacturing of short fibers from almost any fusible material. To this end, a rotating wheel with a notched surface is placed over a melt pool. The rotating extraction device is water cooled and thus generates a high solidification rate. As a result, homogenous distribution of the alloying elements, small grain size, reduced segregation and extended solubility, as well as the formation of metastable phases is achieved. More details about the fiber processing route can be found in [1].

In order to obtain foam-type gold structures, the Schwartzwalder process was employed [2]. Prior to coating, the closed-cell PU foam is reticulated, meaning that the cell walls are removed by means of an explosion reaction, this way turning the foam into an open-cell sponge. The sponge is subsequently coated with a slurry that contains a binder and a high load of metal powder particles. Care has to be taken with regard to the rheological properties of the slurry. After coating, optional shaping operations like bending or cutting can be carried out prior to the heat treatment. Debindering is usually carried out in hydrogen-containing atmospheres. After removal of the organic constituents, sintering leads to a rigid sponge with hollow struts. More details about this process can be found in [3].

Hollow spheres and hollow sphere structures start from coated EPS spheres. Again, a slurry containing a binder and gold powder has to be prepared. The EPS spheres are kept in a fluidized bed and spray-coated with the slurry. This time, the rheology has to be optimized for the spraying process. As an option, the single green spheres can be further processed in the unsintered state to yield a

*Corresponding author. Andersen, O. (olaf.andersen@ifam-dd.fraunhofer.de)

 http://dx.doi.org/10.1016/j.mprp.2017.06.002

Please cite this article in press as: O. Andersen, et al., Met. Powder Rep. (2017), http://dx.doi.org/10.1016/j.mprp.2017.06.002

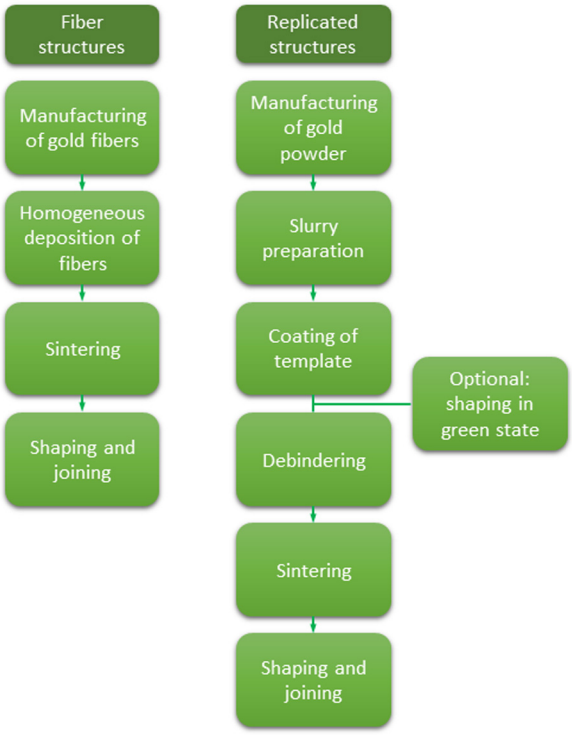

FIGURE 1

Basic processing sequence of the methods used.

shaped body consisting of many slightly deformed spheres that can be heat-treated as a whole. This way, either single hollow gold spheres or hollow sphere structures can be obtained. More details about this manufacturing route are given in [4].

Determination of favorable sintering conditions

A literature survey on sintering of gold alloys was conducted, the most relevant findings of which are discussed below. [5] reports on the powder metallurgical production of wedding rings made from 9 ct. gold alloy (37.5 wt% Au, rest Ag, Cu, Zn and others). In order to prevent Cu and Zn from oxidizing, a controlled oxygen-free atmosphere is recommended. Sintering was carried out 20 degrees below the solidus temperature at 780 °C for 24 h in an atmosphere comprised of 95% N_2 and 5% H_2 with good results.

The production of metal injection molded parts from 18 ct. gold alloys is reported in [6]. In comparison with precision-cast parts, the obtained microstructure is much finer and, thus, provides better properties. Debindering and sintering takes about 65 h. From the diagrams provided in the paper, it can be deduced that the sintering time amounts to roughly 24 h. According to the authors, sintering was carried out at a temperature of 80–90% of the melting temperature. The quasi-binary phase diagrams for an 18 and a 14 ct. gold alloy are reproduced in Fig. 2 were redrawn from diagrams given in [7]. The diagram for the 18 ct. alloy indicates that the sintering temperature used in [6] would clearly correspond to solid state sintering.

The sintering atmosphere consisted of 80% Ar and 20% H_2. Like other authors, [6] acknowledges the role of the gas flow and recommends low mass flows in order to warrant homogeneous temperature conditions throughout the samples. Problems with remaining porosity are explained in terms of inhomogeneous packing of the powder particles.

The following conclusions were drawn from the literature study:

- Commercial sintering is done in solid state only and requires from 3 up to 24 h of sintering time
- No publication on supersolidus liquid phase sintering has been found
- The majority of the reported sinter atmospheres is composed of an inert gas (either N_2 or Ar) and 5–20% H_2
- The gas mass flow should be low in order to provide a constant temperature throughout the samples
- For the quasi-binary phase diagram Au-Cu-Ag for an 18 ct. gold alloy with a silver content of 12.5 wt% as used in this work, the temperature interval between the solidus and liquidus temperature amounts to roughly 30 K. This is sufficient for controlled supersolidus liquid phase sintering with approx. 20–30 vol% of liquid phase and should result in a drastic reduction of the required sintering time. Additionally, large sinter necks between the single fibers were expected and hence a good stability of the sintered fiber structure. When starting from fine particles, sintering to full density is expected to happen much faster than with solid state sintering
- The quasi-binary phase diagram Au-Cu-Ag shows for a 14 ct. gold alloy with a silver content of 15 wt% as used in this work that there is a temperature interval of also roughly 30 K between the solidus and liquidus temperature. This is even more convenient for controlled supersolidus liquid phase sintering as compared to the case of the 18 ct. alloy.

Therefore, supersolidus liquid phase sintering was preferred over solid-state sintering in order to produce the desired structures.

Manufacturing of porous gold fiber structures

The goal of this development was to manufacture porous 18 ct. gold structures with a total porosity of approximately 60%. At sufficiently large length-to-diameter ratios of the fibers, a high degree of porosity can be achieved due to the low tap density of the deposits made from such fibers. The single fibers should then be joined by sintering in order to produce a stable, rigid porous gold structure that is suitable for a subsequent milling step.

The melt extracted fibers typically show a sickle or kidney shaped cross-section. In the case of 18 ct. yellow gold, finally fibers were obtained with the parameter values given in Table 1. The mean equivalent diameter corresponds to the diameter of a hypothetical fiber with a circular cross section and the same length and weight as the measured fiber. The length distribution of the fibers was determined via an optical scanner method, whereas several hundred metallographic fiber cross sections were evaluated via image analysis for the determination of the equivalent diameter distribution.

The cross sections were also subjected to an etching treatment in order to visualize the microstructure of the as-extracted fibers (Fig. 3).

TABLE 1

Properties of melt extracted gold fibers.

Sample no.	Mean equivalent diameter (metallography) (μm)	Standard deviation of diameter (metallography) (μm)	Mean length (mm)	Standard deviation of length (mm)
V644/1	95.7	27.1	5.0	1.2
V644/2	83.3	35.6	5.1	1.1
V644/3	68.9	18.9	5.2	0.9

Please cite this article in press as: O. Andersen, et al., Met. Powder Rep. (2017), http://dx.doi.org/10.1016/j.mprp.2017.06.002