Melt Extraction of Gold Fibers and Precious Metal Doped Fibers and Preparation of Porous Gold Fiber Structures

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Abstract

Crucible melt extraction yields short metal fibers with eqivalent diameters as low as 50 µm from almost arbitrary metals and alloys. Highly porous components can be made from such fibers by suitable deposition and sintering methods. This technology is being developed at the Dresden based Department of Powder Metallurgy and Composite Materials of the Fraunhofer Institute for Manufacturing and Advanced Materials (IFAM) and has been applied to gold alloys and iron-base alloys containing small additions of precious metals.

From the manufactured gold fibers, sintered structures were made for decorative applications. Additionally, it was found that due to rapid solidification during the fiber formation, precious metals can be finely dispersed in iron-chromium-aluminum (FeCrAl) and FeAl20 alloys. Good catalytic activity at elevated temperatures was found in compositions containing 3 wt.-% Ce and 0.5 wt.-% Pt.

1. Introduction

In the past years, a new approach towards highly porous metal components has been under development at the Dresden based Department of Powder Metallurgy and Composite Materials of the IFAM. The components are made from melt extracted metal fibers, where the consolidation of the porous structure is achieved by sintering. Interest in such open-porous structures arises mostly from functional high-temperature applications. Accordingly, components with porosities of 50 to 95 % were manufactured from intermetallics and superalloys like Ni_3Al and FeCrAl, respectively. Depending on the type of application, they were made in different shapes such as flat plates for heat shielding or tube-shaped filter candles for hot gas filtration.

Using the crucible melt extraction process (**Fig. 1**), it is possible to make short fibers from almost any fusible material (1). 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 sizes, reduced segregation and extended solubility, as well as the formation of metastable phases is achieved. The melt extracted fibers typically show a sickle or kidney shaped cross-section.

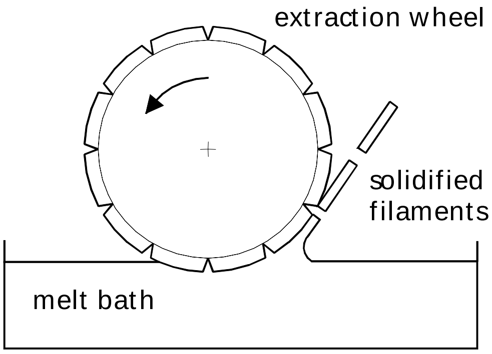

FIGURE 1. Schematic drawing of the crucible melt extraction process

IFAM Dresden has improved the crucible melt extraction process to produce fibers of a mean equivalent diameter from 50 to 150 µm in batch sizes of one to several kilograms. The fiber length can be set from 3 to 25 mm with a deviation of approximately ± 15 %.

Plates, rings, and cylinders can be manufactured from the fibers by depositing them on a suitable sintering substrate, followed by sintering and machining to the desired dimensions (**Fig. 2**). The porosity of these structures can be anywhere between 70 and 95 % and is completely interconnected, allowing for free through-flow of fluids. The pore size is ususally between 10 and 250 µm, depending on the porosity and the fiber diameter.

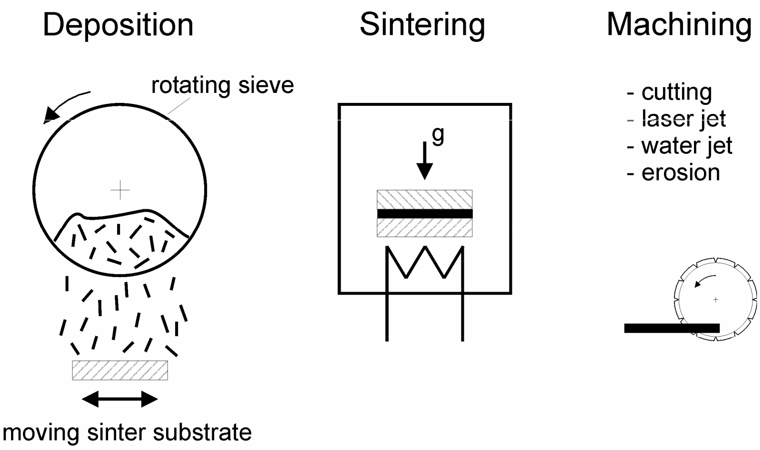

FIGURE 2. Manufacturing of fiber structures

Alternatively, cold isostatic pressing can be applied in order to manufacture filter cartridges. The porosity of these structures is comparably low and amounts to only 50 % (2).

Potential applications are mainly utilizing the functional properties of the sintered fiber structures. Examples include high temperature filtration, flame stop elements, catalyzer substrates, heat shielding, radiant burner surfaces, or heat regenerators. **Fig. 3** shows examples of ongoing research work. Properties with regard to the aformentioned applications are given elsewhere (3).

Heat Regenerator Flame Arrestor Filters Abradable Seals

FIGURE 3. Examples of current research work

2. Melt extraction of 18 ct. gold fibers

The melt extraction of 18 ct. gold fibers was carried out in a closed vessel using argon as the protective atmosphere. Since the required fiber diameters were comparably large, the temperature of the melt could be kept slightly above the melting point, thus minimizing the risk of evaporating zinc. The production rate for these fibers was around 10 to 15 kg/h. For smaller diameter fibers, which would require higher operating temperatures, a recently built plant can be used that allows continuous feeding of the crucible and an over-pressure of 10 bar during operation (**Fig. 4**).

FIGURE 4. New IFAM melt extraction plant allowing for over-pressure of 10 bar

Table 1 shows the results of image analysis size measurements. The equivalent diameter is calculated from the cross section of a fiber assuming that the measured cross sectional area belongs to a perfectly cylindrical fiber. Altogether, a total number of 137 fibers was examined for this analysis.

TABLE 1. Image Analysis Results for 18 Ct. Gold Fibers (Lot V465)

Mean Eqivalent Dia. (µm)	Std. Deviation (µm)	Minimum Eqivalent Dia. (µm)	Maximum Eqivalent Dia. (µm)
202	60	63	396

Fig. 5 shows an etched cross section of a fiber, indicating the typical melt extraction features:

- fine grained structure at the site of contact with the cooled extraction wheel (concave side)
- cristallites oriented in the main direction of solidification.

Aqua regia was used as etchant for visualizing the grain structure.

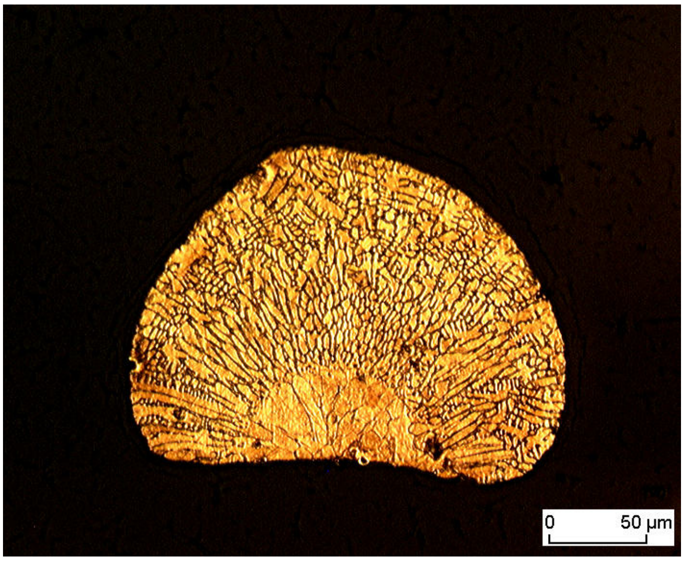

FIGURE 5. Etched micrograph of a 18 ct. melt extracted gold fiber

3. Manufacturing of porous gold fiber structures

In the past, the company C. Hafner GmbH of Pforzheim, Germany, used IFAM made gold fibers for producing sintered fiber webs for jewellery (**Fig. 6**). Lately, the company J. Heinz GmbH, also of Pforzheim, Germany, continued this work and commissioned 18 ct. gold fiber structures. This time, the sintering was done at IFAM, using high processing temperatures combined with short holding times under argon protective atmosphere. **Fig. 7** shows a cross section of a sintered fiber mat which has a porosity of about 95 %. The etched cross section in Fig. 8 shows a significant grain coarsening due to the sintering process.

FIGURE 6. Sintered fiber mats for jewellery made from melt extracted 18 ct. gold fibers (C. Hafner)

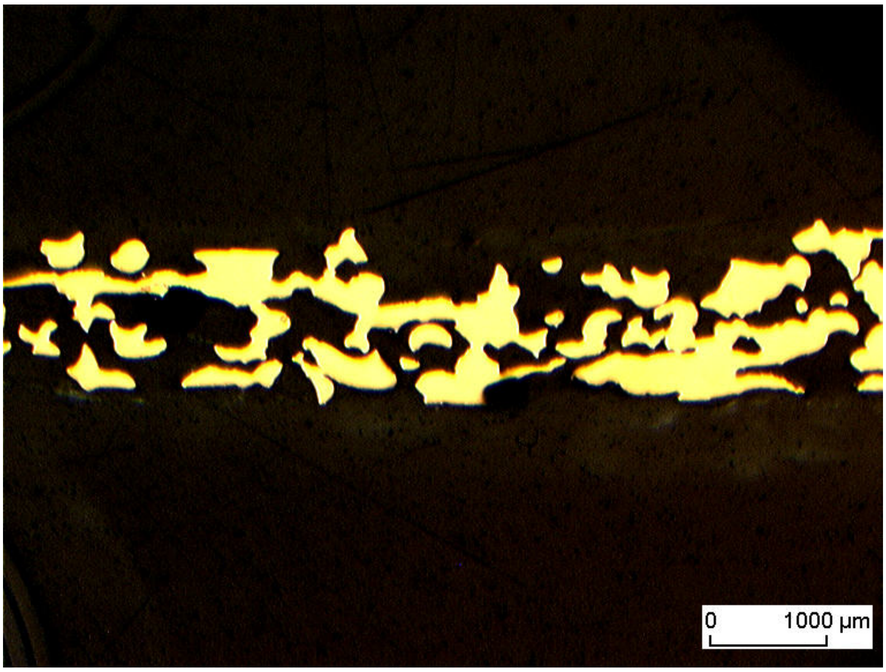

FIGURE 7. Cross section of sintered fiber mat made from melt extracted 18 ct. gold fibers (IFAM)

FIGURE 8. Etched cross section of sintered fiber mat made from melt extracted 18 ct. gold fibers (IFAM)

4. FeCrAl alloys doped with precious metals

Due to rapid solidification during the fiber formation it can be expected that alloy components will be evenly distributed across the fibers. **Fig. 9** shows an EDS line scan across a metal fiber made from Fe -20Cr - 5Al - 0.1Y - 0.5Pt - 0.5Rh after annealing in air for 500 hrs at 1000 °C. The line scan reveals a sharp drop of Fe where it touches upon a large Rh precipitate. Pt seems to be evenly distributed across the fiber. At the surface of the fiber a steep increase of Al ist measured which is caused by the formation of the protective aluminum oxide layer. The formation of the oxide layer causes diffusion of Al from the inside to the surface of the fiber.

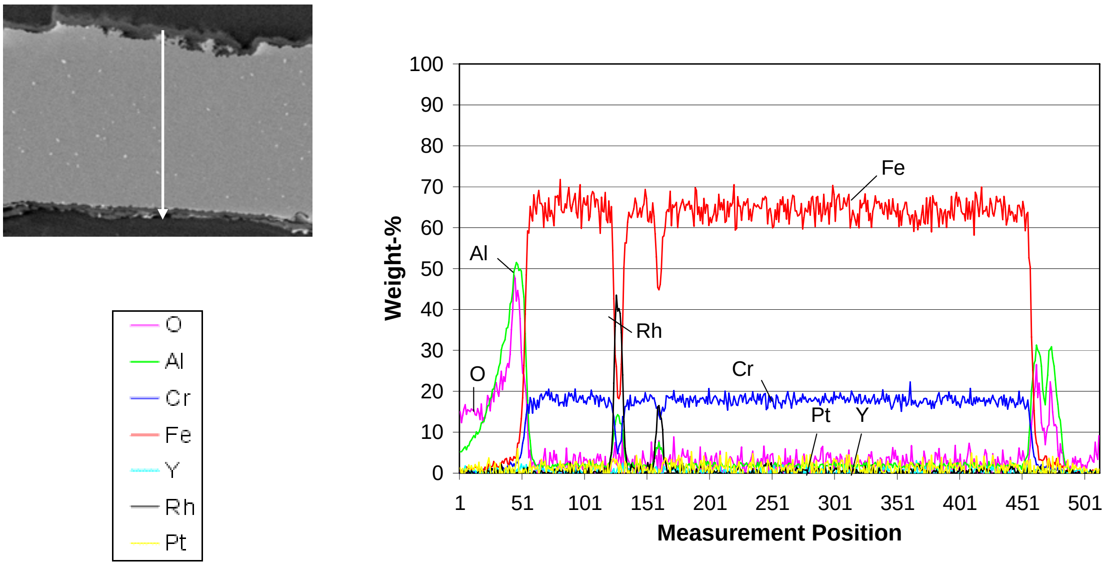

FIGURE 9. EDS line scan across an annealed Fe -20Cr - 5Al - 0.1Y - 0.5Pt - 0.5Rh fiber

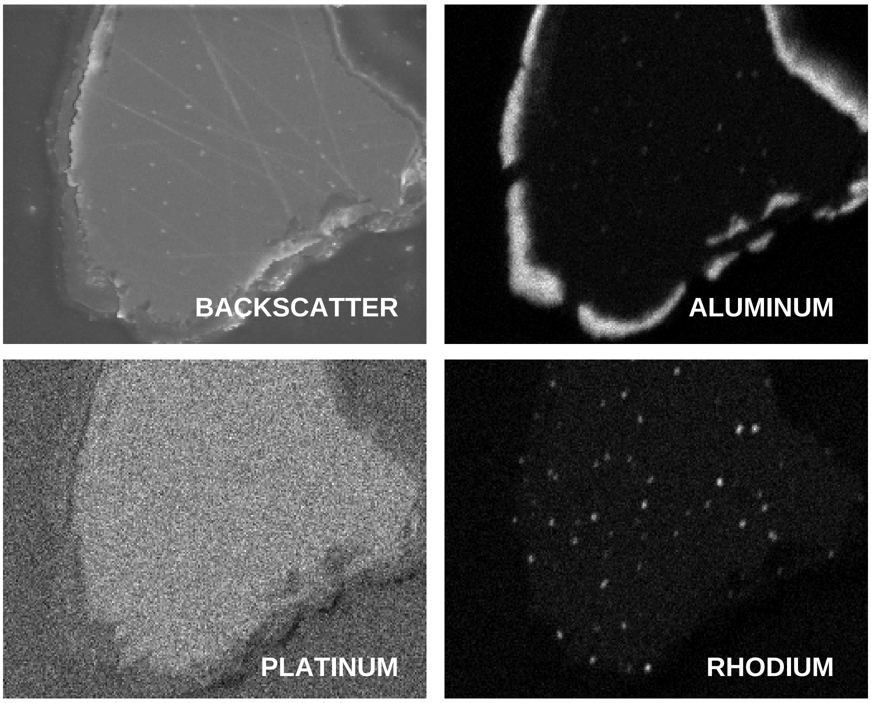

FIGURE 10. Elemental distribution of an annealed Fe -20Cr - 5Al - 0.1Y - 0.5Pt - 0.5Rh fiber

The elemental distribution across a fiber is shown in **Fig. 10**. The measurements confirm the above findings and show evenly distributed Rh precipitates and finely dispersed Pt in the matrix as well as the expected aluminum oxide layer (4). Actually, the size of the precipitates does not markedly increase by the annealing treatment. These findings also hold for Pd which behaves very much like the Rh additions.

It was found that the catalytic conversion of nitrogen oxides (NO) and hydrogenated carbons (HC) was unsatisfactory for FeCrAl based compositions. Since it was speculated that the high chromium content could be detrimental to the catalytic activity, the base composition was changed and an iron aluminide FeAl20 was chosen where also some Ce was added in order to improve the oxygen storage behavior. New tests showed a significantly improved conversion behavior (**Fig. 11**), although light-off temperatures remained about 150 to 250 °C higher than those of conventional washcoated catalyzers. However, the addition of Ce caused a notable drop in the oxidation resistance of the fibers.

The specific surface area of the melt extracted fibers is small in comparison to the washcoated catalyzers normally used for total oxidation. Therefore, conversion rates at the same temperature are significantly lower. However, in harsh environments that are characterized by thermal shock, high temperatures and possibly abrasive dust that may wear off the washcoat, directly doped fibers could be an alternative to washcoated structures. Additionally, it is possible to produce highly porous structures from these fibers that create a turbulent flow pattern and thus enhance the catalytic conversion.

The specific surface area of the fibers is usually in the range of 0.005 to 0.02 m^2/g, depending on the actual mean diameter of the fibers. It was found that for selective oxidation processes, these values lie in a very favorable range. Fibers made from tailored alloys can bring about a very good performance in certain model reactions such as the selective oxidation of propane (5).

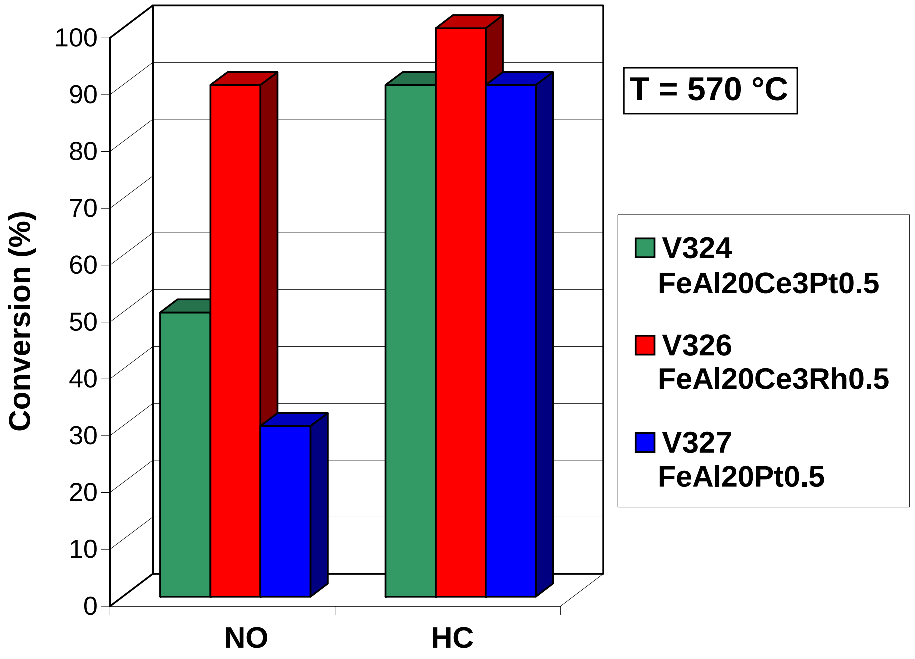

FIGURE 11. Conversion of nitrogen oxides (NO) and hydrocarbons (HC) in dependence of different fiber compositions

5. Conclusions

Melt extraction can be used to make short fibers from precious metals or alloys which contain precious metals in varying amounts. Highly porous structures for decorative applications were manufactured from 18 ct. gold fibers by suitable deposition methods followed by a sintering treatment.

In iron-chromium-aluminum and other iron-base alloys, rapid solidification leads to a homogenous distribution of small additions of precious metals. Rhodium tends to build comparably large precipitates after annealing in air at 1000 °C for 500 hrs, whereas Pt remains finely dispersed in the matrix. At elevated temperatures, good catalytic activity with regard to hydrocarbon and nitrogen oxide conversion was found for a FeAl20 composition containing 3 wt.-% Ce and 0.5 wt.-% Pt.

6. Acknowledgements

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