Sinterpaper – A New Type of Highly Porous Material

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Introduction

Porous metals and alloys have gained more and more attention during the last two decades. The increasing interest in porous metals is due to the fact that the material is characterized by interesting combinations of physical, chemical and mechanical properties. These highly porous materials also possess combinations of properties which are not possible to achieve with other materials. Beside the drastic weight and materials savings that arise from the porous structure, there are also other application-specific benefits such as noise absorption, heat insulation, filtration effects, mechanical damping and energy absorption. Because of the high specific surface area highly porous metals are excellent candidates for catalytic applications.

Porous metals and alloys can be manufactured by several methods. The common way is the filling of metal powder into appropriate dies with subsequent compacting in an axial direction by mean of an upper and lower ram. In a second step an additional sintering procedure is applied to fulfil the required properties. The pore size and the total porosity of the finished product can be controlled by the choice of powder size, the pressing force and the sintering conditions. A wide range of geometries and shapes can be obtained by mean of this pressing process [1].

For the manufacturing of bigger parts like filter candles isostatic pressing, with a low pressing force will be used [2].

For the processing of porous sheets and foils two methods have developed to date, the powder rolling and the tape casting technology. The powder rolling method is characterized by feeding of metal powder between a pair of horizontal cylindrical rolls, which compact the powder into a continuous strip having sufficient mechanical strength of further handling. The compacted strip is next sintered at a desired temperature [3-6]. The as sintered strip is characterized by a porous structure. Typical sheet thicknesses are in the range between 0.5 and 2 mm, whereas the width is between 50 – 200 mm. Because of the mechanical deformation within the roller gap powders with an irregular morphology are preferred.

Nowadays powder rolling will be used for the production of small quantities of special materials such as cobalt- or nickel-base alloy sheets for welding, nickel-iron sheets for controlled expansion properties, special Cu-Ni-Sn alloys for electronics and porous nickel sheets for alkaline batteries and fuel cell electrodes or composite bearings [8].

The tape casting technology is characterized by feeding a metal powder consisting slurry from a storage container onto a plastic foil, which is continuously dragged with a controlled velocity under the container. The high of the slurry is controlled by an s.c. doctor blade, which determine the final layer thickness. The as formed metal sheets have to be dried and additional sintered [9-10]. The porosity of the sheets can be controlled by the particle size, particle morphology and especially by the sintering temperature [11]. For sheets with a porosity > 50 % additional organic space holders are necessary.

Using tape casting typical sheet thicknesses ranges from 0.2 – 1 mm whereas the width can be varied between 20 and 300 mm.

The present paper describes a new technology for manufacturing of thin highly porous metal sheets called sinterpaper using a new technological approach.

Experimental

The new technology consists of a combination of paper and sinter technology. Nowadays common paper is characterized by a composition of cellulose fibres, filler like Kaolin or Barite and some additives. The filler will be used to reduce the amount of cellular fibres in the paper as well as to influence different properties of the paper like printability, whiteness, surface roughness etc. Within the new technological approach the filler of the conventional paper has to be replaced by metal powder and in some cases by metal fibres, see the technological approach in Figure 1 [12].

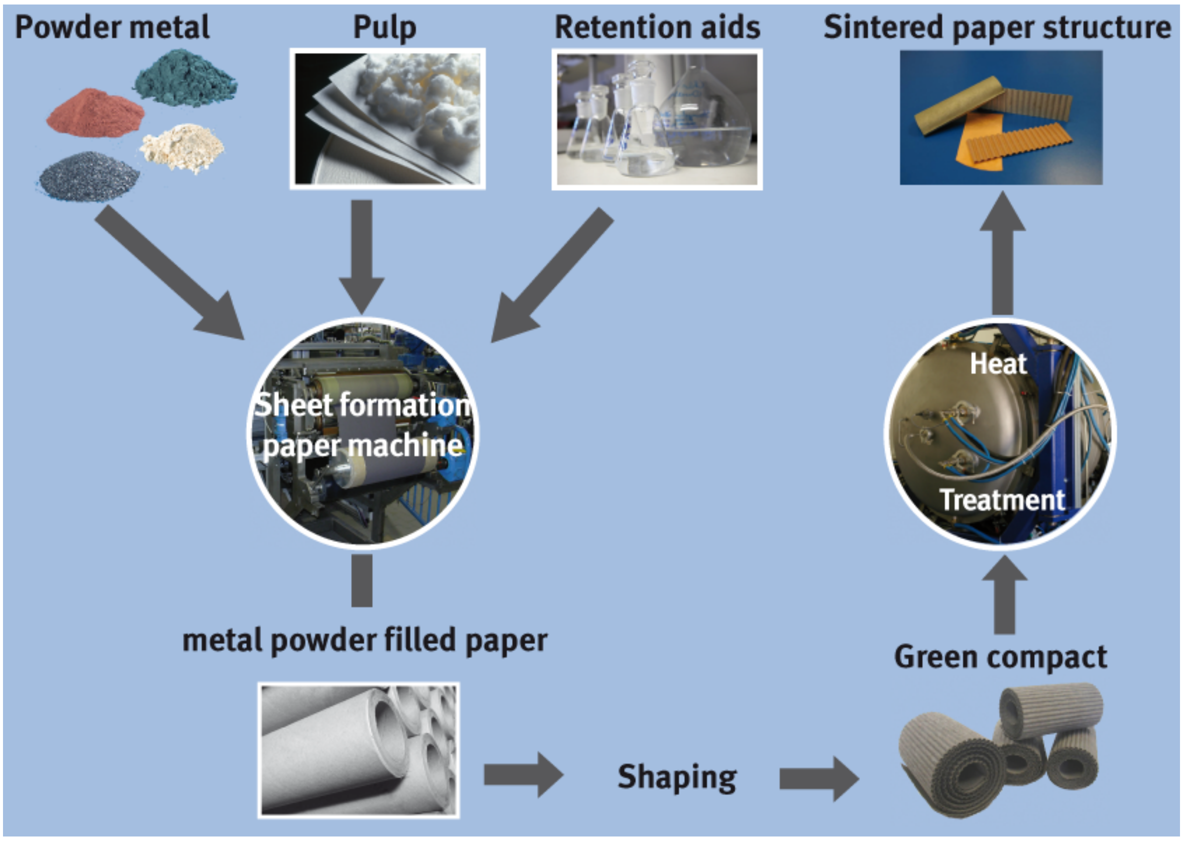

Figure 1 Technological steps for the manufacturing of sinterpaper

For this investigation two types of metal powder have been chosen: 316L-powder, d_{50} ~ 10 µm, spherical morphology (from ATMIX Corp., Japan) and Cu-powder, d_{50} ~ 5 µm, spherical morphology (from ECKA Granules, Germany). Furthermore for some trials the influence of 316L-fibres, ~ 10 µm diameter, length ~2 mm (from Bekaert, Belgium) has been selected. The amount of powder has been varied to 75, 82 and 88 wt.% which represents ~ 35, 45 and 55 vol.% of metal within the paper composition. The rest consists of cellulose fibres (~ 20 – 30 µm diameters) and some special additives for the paper manufacturing.

The metal powder contained paper has been prepared using a paper sheet device (called Rapid Köthen) which allows a high flexibility in order to vary the composition, the content of metal powder and cellulose fibres as well as paper formation additives. Additional some as fabricated metal powder filled paper (“green sinterpaper”) has to be treaded by some shaping operations like folding, winding or corrugation.

The heat treatment was performed as following two steps, i. e. debindering to remove the organic constituents and sintering to attain the final properties. For the stainless steel sinterpaper the debindering temperature was selected at 600 °C under an atmosphere of Ar/H_2-mixture for 1 h whereas the copper sinterpaper has to be debindered at 500 °C in air for 1 h. The sintering procedure was carried out for both materials under hydrogen atmosphere for 30 minutes while the temperature was varied in a wide range, i. e. between 550 – 900 °C for copper and 100 – 1250 °C for 316L.

The average density and the shrinkage behaviour of the green as well as sintered sinterpaper were determined by measuring the dimensions of the sheet by a micrometer and weighing each piece. Porosity was characterized by means of a helium pycnometer (AccuPyc 1330, Micromeritics, U.S.).

Tensile tests were performed using a mechanical testing machine (Zwick 1476, Zwick GmbH, Germany) with a 1 KN load cell at a velocity of about 1 mm/min.

Results and discussion

Sinterpaper formation

Figure 1 show typical sinterpaper based on stainless steel and copper. Successful manufacturing of metal powder filled paper could be demonstrated in a thickness range between 0.2 – 0.7 mm. A critical issue in the preparation of metal powder filled papers is the strong difference of the density of the metal powder compared to the cellulose fibres with normally leads to a significant sedimentation of the metal powder.

Figure 2 Sinterpaper based on stainless steel and copper

Therefore strong efforts in the development of useful slurries for the sinterpaper formation have to be carried out. Additional trials in shaping of the green sinterpaper like folding, winding or corrugation have shown nearly the same behaviour like common paper with the equal thickness, see also Figure 2.

A cross section of a stainless steel powder filled paper is seen in Figure 3, which reflects the distribution metal powder of the cellulose fibres.

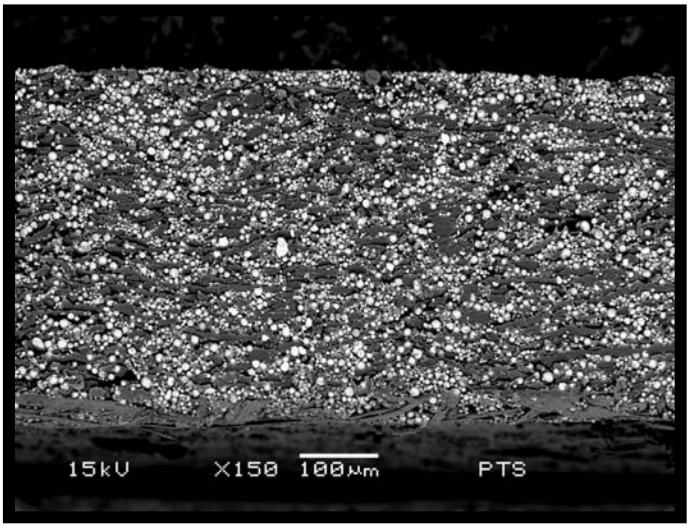

Figure 3 SEM image (cross section) of the green sinterpaper based on stainless steel 316L

After burnout of the organic constituents, which was complete at 600 °C an open porous structure of the sinterpaper could be observed, see Figure 4.

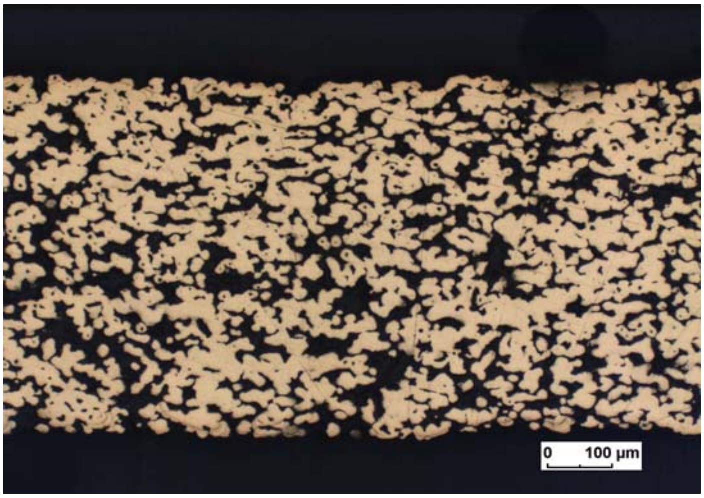

Figure 4 Metallografic picture (cross section) of a copper sinterpaper

Dimensional change after sintering

The dimensional changes of the green sinterpaper have been examined with respect to length, width and thickness. As demonstrated in Figure 5 for the 316L sinterpaper the shrinkage in length and width direction is as expected and is increasing with rising sintering temperature. Additionally with decreasing of the metal powder content the shrinkage is increased. An unexpected swelling behaviour was obtained after examination of the thickness. The reasons could be a spring back effect (relaxation) of the cellulose fibres during debindering (300 – 500

°C) of the green sinterpaper. Furthermore the shrinkage in width and length direction could shift the coarse pores into z-direction.

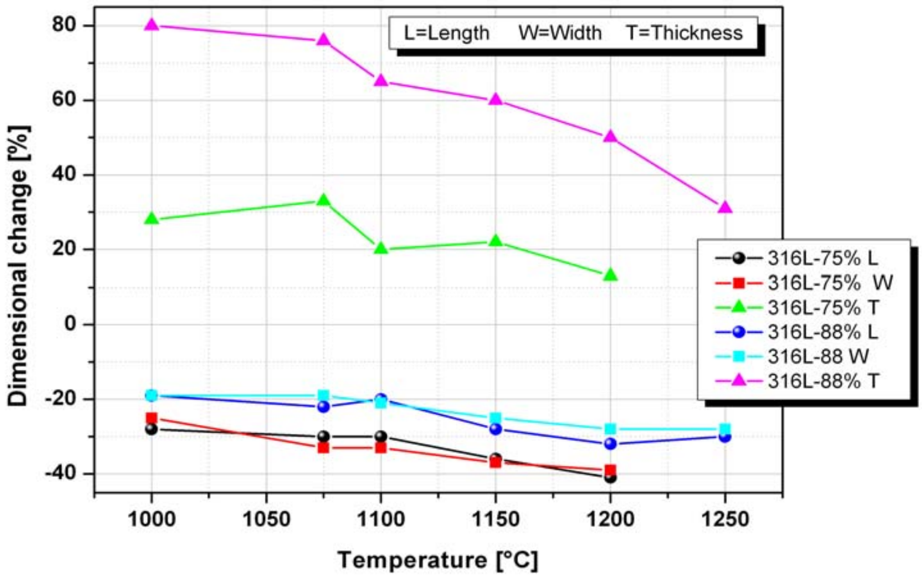

Figure 5 Dimensional change of 316L sinterpaper in dependence of the sinter temperature and the amount of powder (75, 88 wt.%)

For the Cu sinterpaper (Figure 6) the shrinkage behaviour is as expected, i.e. the thickness reveals a significant densification esp. for the Cu-75 wt. % sinterpaper. An explanation could be the mechanical deformation of the soft copper particles which avoid any spring back effect of the cellulose fibres. Additional because of the mechanical activation of the copper powder the shrinkage in all directions occur.

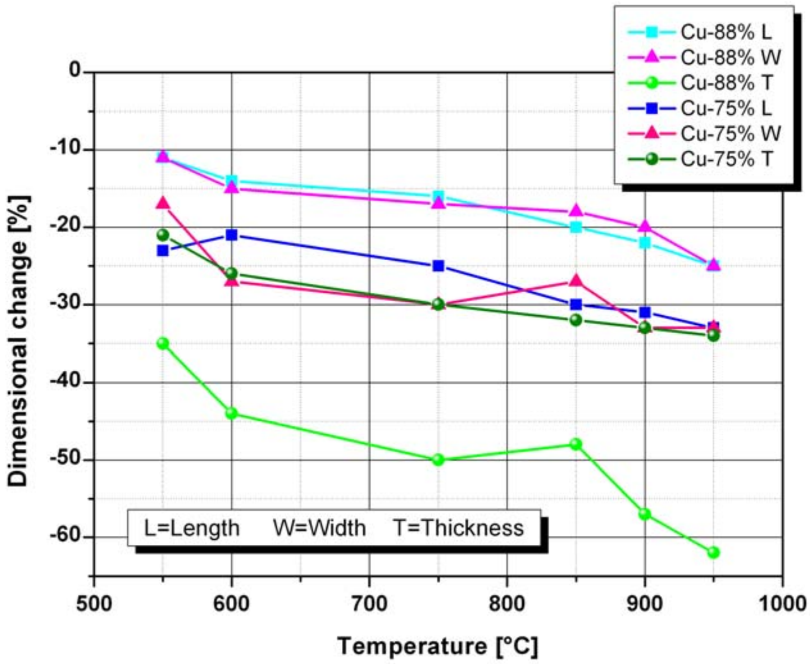

Figure 6 Dimensional change of copper sinterpaper in dependence of the sinter temperature and the amount of powder (75, 88 wt.%)

Porosity and pore size

The porosity of the sinterpaper can be controlled in a wide range by the sinter temperature for copper as well as 316L-sinterpaper, as demonstrated in Figure 7a, b.

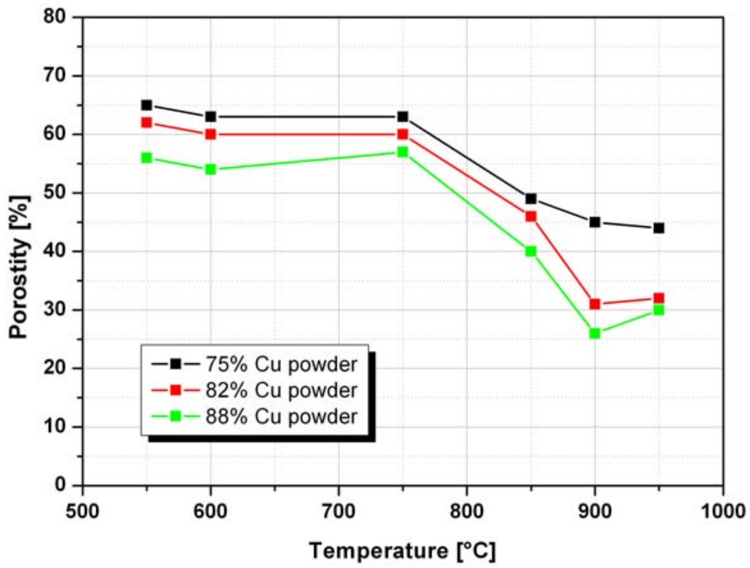

Figure 7a Porosity of copper sinterpaper in dependence of the sinter temperature and the metal powder filler content

For the copper sinterpaper an additional influence of the degree of the amount of the filler can be observed, means a higher cellulose fibre content led to an increased porosity of about 5-10% independent of the sintering temperature. For the 316L-sinterpaper those expected behaviour couldn't be detected so far.

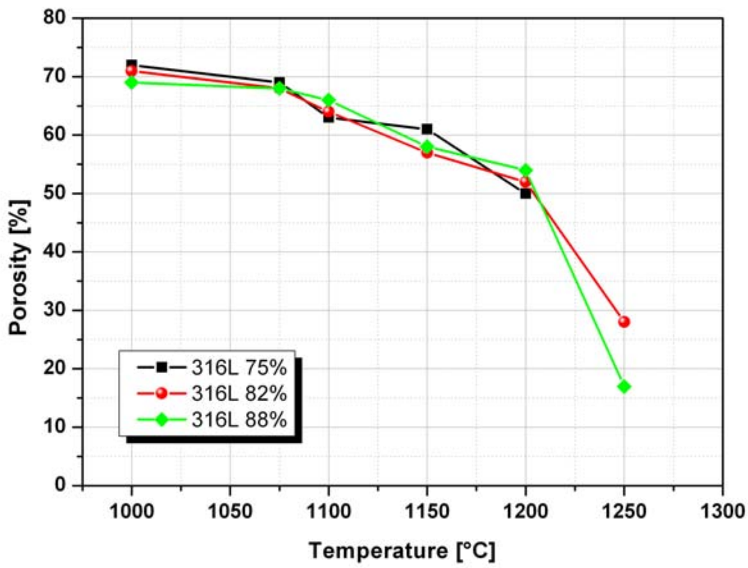

Figure 7a Porosity of 316L sinterpaper in dependence of the sinter temperature and the metal powder filler content

The pore size of the sinterpaper is characterized by two types, i.e. coarse longish pores with dimensions in the range between 100 – 300 and pores less than 20 µm. The coarse pores represent the shape and geometry of the cellulose fibres whereas the fine pores reflect the spaces between the powders, which can be significantly influenced by the sintering temperature.

Mechanical properties

The tensile strength of the 316L-sinterpaper ranges from nearly 20 MPa to 270 MPa. As seen in the Figures 8a, b a tremendous influence of the sinter temperature on the strength and strain behaviour have been obtained.

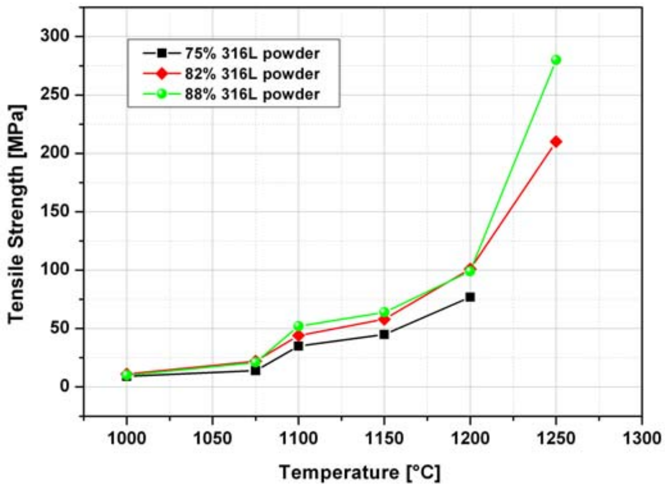

Figure 8a Tensile strength of 316L sinterpapier as a function of the sinter temperature and the metal filler content

The significant loosening of strength and ductility is attributed and directly controlled by the behaviour of the porosity. Additional the influence of the amount of the metal powder filler content could be observed and reveal that with increasing the powder metal content the highest strength value have been attained.

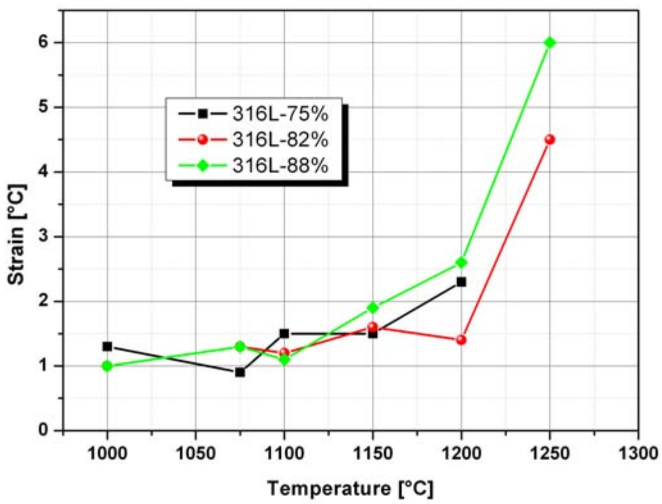

Figure 8b Strain of 316L sinterpapier as a function of the sinter temperature and the metal filler content

Summary and outlook

A new technological approach for manufacturing of porous thin sheets the s. c. sinterpaper has been developed. The manufacturing consists of a combination of paper and sinter technology. Sinterpaper in the thickness range between 0.2 and 0.7 mm have been prepared, whereas the porosity level can reach up to 75 %. The pore size has a bimodal character, i.e. longish coarse pores of around 200 µm and small pores less than 20 µm. Investigations of the sinter temperature have shown a significant influence on the porosity as well as on the mechanical properties.

The new technology for sinterpaper manufacturing has some advantages like materials flexibility, thin sheet manufacturing, simple shaping and after treatment (like plain paper), variation in length and width and tailoring of the pore size, pore size distribution and total porosity.

The process can be up scaled and is characterized by low cost processing.

Based on the advantages above numerous fields of potential applications can be selected. Filters for gases, liquids and particle should be one of the main fields of applications. Furthermore porous sinterpaper should be applied for thermal insulation, for electromagnetic shielding. Other interesting applications could be electrodes, heat exchanger (heat pipes), vaporizers and evaporators, catalyst substrates and light-weight structural components.

Further investigations and activities are focused in the development of graded porous sinterpaper (membranes). Additional shaped products like corrugated sinterpaper, cardboard and tubes will be developed and tested.

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