Transfer of manufacturing process for stainless-steel foam to industrial scale

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Introduction

Typical Schwartzwalder replica-foams are manufactured by using a reticulated polyurethane-foam, which is impregnated with slurry by kneading and pressed out to homogenize and to cover only the surface of the foam and not the total volume of the unit. Subsequently, they are dried and finally a thermal treatment is performed, during which the polyurethane is burned out and the metal powder is sintered [1,2]. Although this technology is quite simple, only large-scale production for ceramic molten metal filters are known (Selee, Vesuvius, Shengquan and others). This paper describes activities to transfer stainless steel foams from a lab to an industrial scale and focuses on slurry development as well as thermal treatment development and first product applications. Furthermore, characterization methods are described, which were important for the successful development process.

Powder and foam characterization

The aim of this work was to develop coating slurries for foam manufacturing with non-Newtonian shear thinning flow behavior and high solid contents. They should be water based and consist of metal powder and additives which are necessary to glue the particles on the surface of the foams. As basic component an Atmix 316L (1.4404)-powder with an average particle size of 6 µm and a specific surface of 0.36 m²/g was used. This powder is commonly used for MIM-production and fits to cost calculations which have been done before. As shown infigure 1on the left side, the powder morphology is mostly round depending on its production process using gas atomization. Due to its low surface, high roundness and density, it has a high tendency for sedimentation and is hard to process. Compared to a typical silicon carbide powder the dynamic mobility is extremely low (figure 1, right). This induces that powder stabilization is the main task for slurry development and it has to be achieved by steric methods.

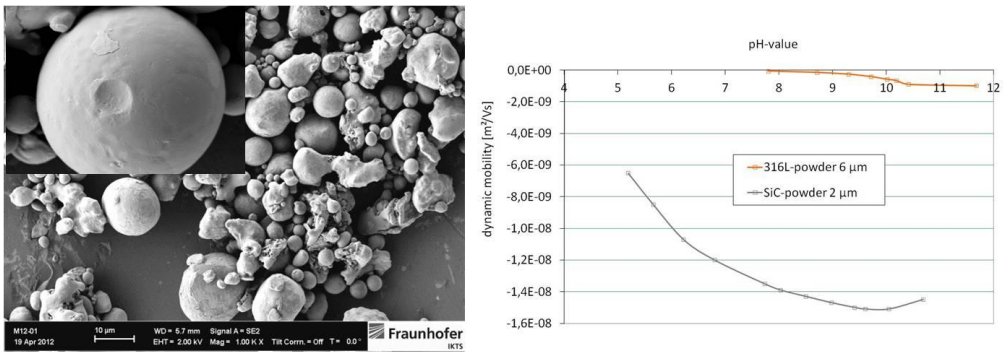


Figure 1: Left: powder morphology of 316L-powder; Right: dynamic mobility of 316L-powder compared to silicon carbide powder

New methods were used for foam characterization, going beyond the typical ppi-classification of ASTM-standard D 3576-77. The new technique uses a special optical method, where only the surface of the foams is lighted [3]. As a result, only the struts on the surface are pictured and it is possible to reconstruct the foam cells. At the end, the equivalent diameter (ecd) of these reconstructed cells acts as measurement value and provides more information about the used material and prospective properties. The measurement technique works very fast compared to 3D-methods like computer tomography, and it was also used for quality control for all foams which were processed.

Scientific development of slurry and coating technique

The described industrialization concept included all polyurethane foam cell sizes commercially available. That fact was important to reach the most variability regarding the tested and prospective applications. For this reason, the foams were classified in two groups, the coarse ones from 5 to 1.5 mm (recipe cf) and the finer ones with 1.2 to 0.4 mm (recipe ff) equivalent diameters. Every group required its own flow behavior and viscosity, which led to different slurry compositions. Initially, rheological measurements using rotation tests were carried out to measure the shear thinning behavior. However, this method is not appropriate to describe the complex viscosity of these steel slurries exactly enough. Only new oscillation measurements brought the decisive breakthrough for finding the right additives and describing their effects on the coating behavior and fixation of the slurry on the foam struts.

Table 1: Composition of coating slurries

	recipe ff	recipe cf
cell sizes	0.4-1.2 mm	1.5-5 mm
types of auxiliaries	mixture of PVA and poly saccharide, polycarboxylate, polyurethane additive	mixture of PVA and poly saccharide, polycarboxylate, polyurethane additive, glucose, silicon oil
amount of auxiliaries	1.2 mass-%	1.7 mass-%
solid content	87.9 mass-%	88.1 mass-%
yield point	3.5 Pa	75 Pa

The composition and some properties of the recipes are summarized in table 1. Both types contain nearly the same additives, whereas recipe cf for coarse foams additionally contains glucose as rheological additive and silicon oil as antifoaming agent. This results in a higher yield point, an important property for foam coating.
For rotation the flow behavior of both slurries is nearly on the same level, only in the region of low shear rates recipe cf has slightly higher values (figure 2,left). With oscillation tests more precise information could be provided about the deformation behavior under elastic and plastic conditions with extremely small shear deformation. The levels of the storage modulus G' and loss modulus G'' could be evaluated and also the yield point could be measured exactly (cross-over point of G' and G''). As result it was figured out that both recipes have higher elastic than plastic components under nearly static conditions. This characteristic correlates to the observed excellent adhesion of the slurry on the foam struts at coating trials. The level of G-modules for coarse foam slurry cf was three times higher compared to ff-slurry and the yield point achieved 75 Pa, which was necessary to achieve homogeneous round and complete coverings (figure 2,right).

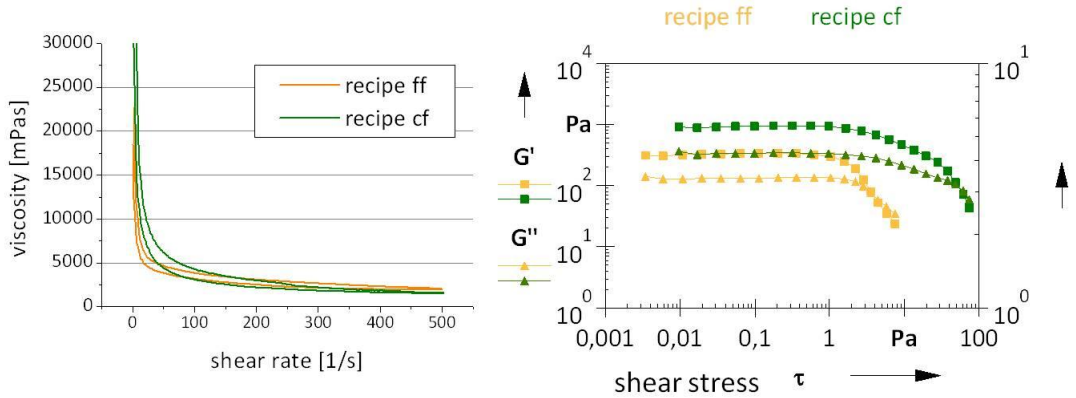


Figure 2: Viscosity measurements (left: rotation, right: oscillation)

The results of coating tests are shown infigure 3. The left coarse foam was coated with cf-slurry and the finer ones with ff-slurry. It could be shown, that all the foam struts are covered completely and the structures are open celled independent of the cell size. Only the finer foams have small amounts of closed cell windows which were acceptable.

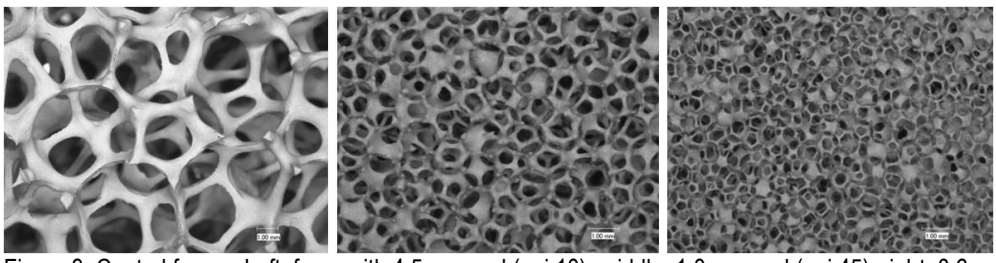


Figure 3: Coated foams; Left: foam with 4.5 mm ecd (ppi 10); middle: 1.0 mm ecd (ppi 45), right: 0.6 mm ecd (ppi 60)

Scientific development of thermal treatment

The thermal treatment development mainly aimed at maintaining the chemical composition of the starting 316L-powder (C<0.03%, Si<1.0%, N<0.11%, 0.045% P, 16.5-18.5% Cr) and the reduction of microporosity, as far as possible. The heat treatment process firstly consists of a debinding step, where PU template, binder and additives are removed. In a second step the metal powder skeleton is sintered.
In order to obtain better understanding of the decomposition of the organic material, the reduction and the decarburization during debinding a new process gas analysis method has been developed. Therefore, a tube furnace was linked with a Fourier-Transform-Infrared (FTIR)-Spectrometer, giving the possibility to detect the composition of debinding gases in situ. This technology allows for a proper and effective parameterization of the heat treatment process. Coated foam samples were

placed in the furnace and heated with different gas compositions and heating rates. As result, the recorded FTIR-spectra give important information on the decomposition of PU-foam and auxiliaries. Best effects were worked out under hydrogen atmosphere. Figure 4 depicts the formation of the mainly appearing gases. The results indicate optimum debinding temperatures of 290 and 340 °C. These temperatures can be associated with the formation of CO_2 and NH_3. Further maxima are detected at 130 and 520 °C, and methane is formed at ~680 °C. Such methane formation correlates to a pronounced decarburization. Finally, the reduction of oxides via formation of CO is detected at temperatures >1100 °C.
The sintering step is carried out at 1250 °C in hydrogen. That way, a high sintering density of the foam struts can be obtained. Higher temperatures lead to slumping effects and should be avoided. On basis of these results the thermal treatment program for batch furnaces was derived and successfully tested.

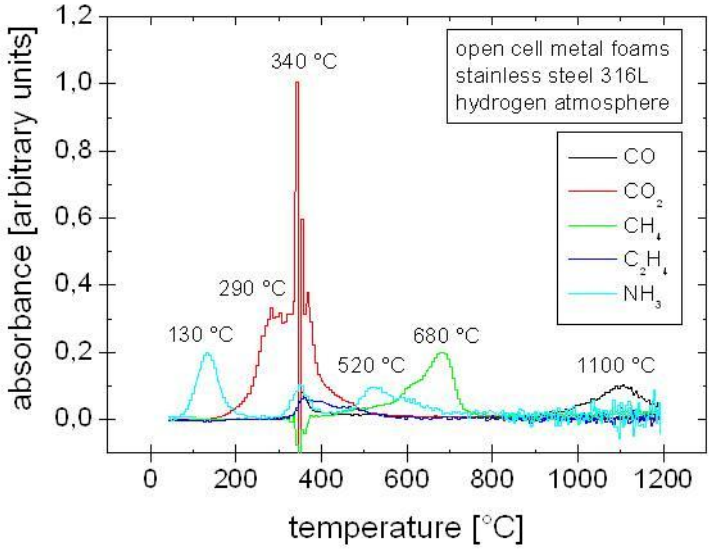


Figure 4: IR Absorption due to the mainly appearing species as a function of furnace temperature

Transfer to Industrial scale
All preliminary examinations were carried out to produce stainless steel foams for industrial applications as coating on heat exchanger tubes and deflector plates. It was important to develop the coating technique as well as the thermal treatment under industrial conditions. Thereby the component dimensions were limited by the size of sintering supports of the used continuous furnace and could be increased easily if larger facilities were available.
As result, foam plates of 280x180x5/20 mm with an ecd of 4.5 mm to 0.4 mm in an amount of up to 150 pieces per cell size were coated and heat treated. Due to the dimensions and number of pieces, which had to be coated, a roller technique was chosen. This impregnation and homogenization method for ceramic foams is mostly used for molten metal filter production. With an output of hundred millions of filters per year, it seems to be the best technology also for steel filter production.
The coating procedure for heat exchangers was less automated. Therefore 8 hollow foam cylinder segments (ecd 3.5 mm) with an inner diameter of 8 and 18 mm, a wall thickness of 4 mm, and a length of 30 mm were covered onto heat exchanger tubes with a length of 300 mm and coated in situ. That gave the possibility to form a direct bonding of the foam coat to the tube, an important aspect for the heat transfer coefficient of the tube-foam composite. The tubes were manufactured in an amount of 450 pieces.
Initially, all thermal treatments were carried out in a batch furnace. After successful sintering the transfer to a walking-beam furnace took place. This concept has a separate debinding area, which was comparable to the preliminary tests, where debinding and sintering were also separated. Pure hydrogen also was used as atmosphere in the sintering zone. For the first trial some problems with shrinkage were noticed, which represented in crack networks. Thus, the temperature in the front area of the furnace and in the debinding area was reduced by 50 K and process time was increased by 25%. With these measures, the debinding was complete before the foams went to sintering zone and got the high quality as shown in figure 5. The final sintering temperature was 1330°C and slightly higher than in batch furnaces.

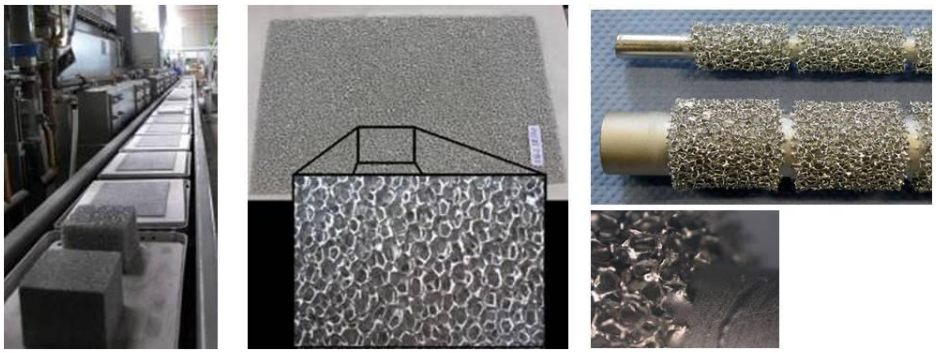
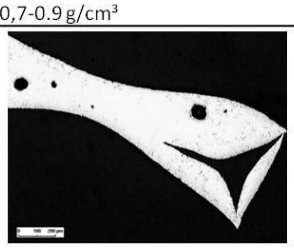
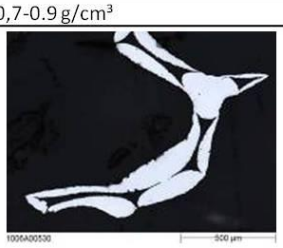


Figure 5: Industrial walking beam furnace with foam tiles and examples of research program (middle: tiles for deflector plates, right: heat exchanger tube with excellent bonding)

Comparison of properties

Due to the diversity of the furnaces, it was interesting whether the results of the scientific thermal treatment development could be implemented in an industrial process. Table 2 compares the results of properties of both processes. The carbon, nitrogen and oxygen contents are nearly similar and comparable to the original alloy definition. Both, shrinkage and density are on the same level and also the microstructures of the sintered foams are nearly dense for both furnaces. Thus, it can be assumed, that the technology transfer to large scale was excellent.

Table 2: Comparison of properties depending on sintering furnace

	Batch furnace (scientific)	Continuous furnace (industrial)
chemical composition	C: <0.02% O: <0.017%	C: 0.017-0.032% O: 0.016-0.022% N: 0.083-0.114%
linear shrinkage	14-16%	13-16%
density	0,7-0.9 g/cm³	0,7-0.9 g/cm³
microstructure		

Applications

The foam covered tubes for heat exchangers could be used as sintered. They were welded in a housing (figure 6, right) and tested under gas-gas transfer in comparison to a conventional tube heat exchanger. The thermal heat transfer coefficient with the novel exchanger was about 19% higher, which is mainly due to its four times higher surface.

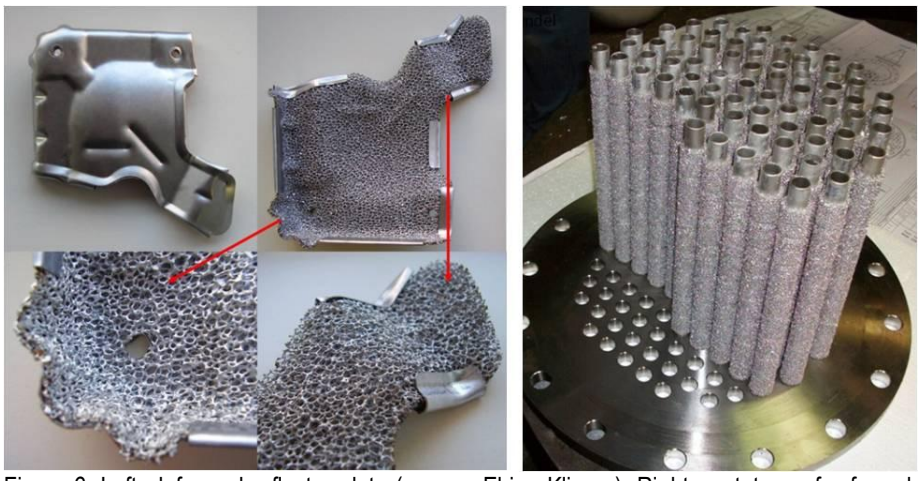


Figure 6: Left: deformed reflector plate (source: Elring Klinger), Right: prototype of a foam heat exchanger (source: Deller GmbH)

For application as deflector plate for thermal and acoustic isolations the stainless steel foams had to be cut with laser beam and deformed together with a metal plate (figure 6, left). Only coarse foams with low carbon contents showed high ductility and could be bent in the needed form. All foams finer than ecs 1.0 mm had cracks at high deformation zones. It is assumed that the struts are too thin for these demands and tend to crack instead of elongation.

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