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A New Class of High Temperature and Corrosion Resistant Nickel-Based Open-Cell Foams**

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A number of nickel-based and iron-based alloys have been successfully developed for applications at high service temperatures and in corrosive environments. Applications such as diesel particulate filters, heat exchangers, and catalyst supports require open-cell porous structures with tailored and uniform material and structural properties, a requirement which can be met by high temperature and corrosion resistant metallic alloy foams prepared with compositions similar to those mentioned above. A new technology that transforms pure nickel foam into an alloy foam, and which has now reached the pilot plant production stage, will be introduced. This technique starts from commercially-available nickel foam, which is uniformly coated with a pre-alloyed powder using standard powder metallurgical methods, and subsequently transformed into the desired alloy throughout the strut cross-section in a relatively short time with a carefully controlled heat treatment that utilizes transient liquid-phase sintering. This process allows for the preparation of a wide variety of foam compositions and structural features, which is important for tailoring material properties to a specific application.

1. Introduction

Applications such as diesel particulate filters, heat exchangers and catalyst supports require open-cell porous structures with tailored and uniform structural and material properties. Mechanical and corrosion stability at elevated temperatures are the most important requirements in the aforementioned applications. INCO is the worlds largest producer of Nickel foam, i.e., over 4,000,000 m² per year are produced, mainly for the battery market. The technology is established for high throughput cost-effective production. However, this foam has only limited high temperature stability. The concept of tailoring the properties of this commercially available foam (INCOFOAM[®]) in order to make it stable at extremely high temperatures could possibly offer a wide range of new applications.

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2. Production Technology

A technology to transform the commercially available Ni foam into an alloyed foam with high temperature stability was developed (INCOFOAM®HighTemp). Fig. 1 shows the patented manufacturing process.^[1-6] The main features of this powder metallurgical process are the coating of the Ni foam with a binder by a spraying process and afterwards with a specified metal powder (e.g. Tab. 2). The following heat treatment includes a debinding and sintering step (see Fig. 2). During the transient liquid phase sintering process elements from the powder diffuse rapidly into the foam struts and ensure a homogeneous alloy foam composition. Microscopy images show a comparison of the pure Ni foam vs. alloyed foam in Fig. 3. The high roughness of the alloyed foam offers a number of advantages, including high specific surface and good adhesion of catalytic coatings which are described in the sections to follow.

In Table 1 a “foam toolbox” summarizing foam properties and their respective ranges is shown. There is a wide range of porosities and pore sizes available in the alloyed foam, allowing filtration characteristics like pressure drop or filtration efficiency to be adapted to the respective conditions. The thickness can be increased substantially by sintering a stack of foams together allowing the manufacturing of geometries like cylinders or cuboids. The process is very flexible with

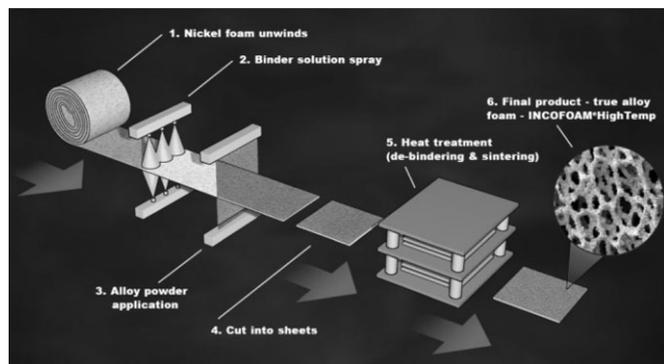


Fig. 1. Manufacturing process for alloyed Ni-based foam (schematic).

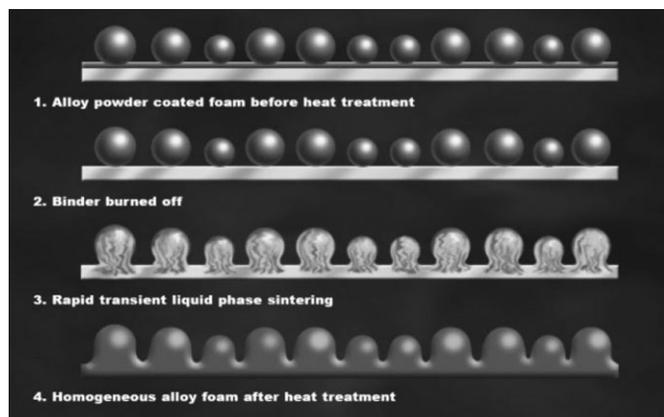


Fig. 2. Schematic illustration of processes occurring during transient liquid phase sintering with increasing temperature and time.

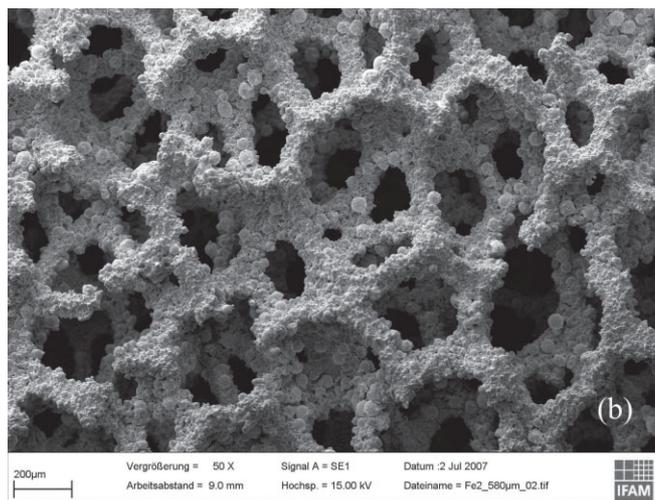
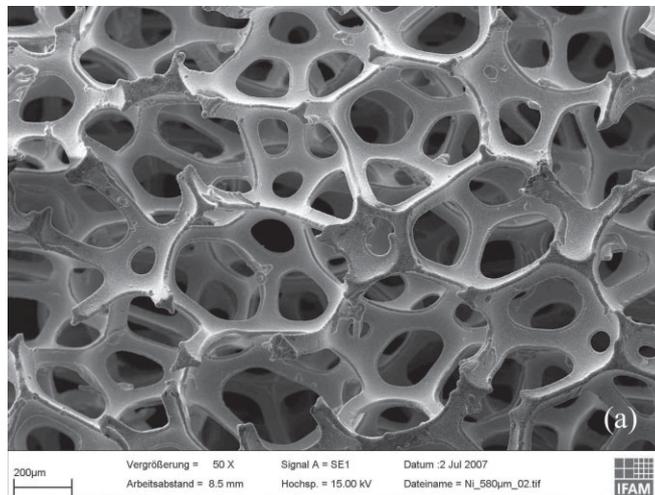


Fig. 3. SEM images of (a) pure Ni foam and (b) alloyed foam.

Table 1. Foam Toolbox.

Properties	Range	Application
Pore size distribution	250 micron to 2 mm	Flow resistance, pressure drop, filtration efficiency as deep bed filter
Porosity	95 % max	Flow characteristics, pressure drop
Density	300 g/m ² to 5000 g/m ² depending on thickness	Mechanical strength, corrosion resistance, durability
Thickness	1 mm to 5 mm (depending on pore size)	Manufacturability, shaping, cost
Alloy composition	Inconel® type, Monel®, NiAl, NiAlCr, FeNiAlCr	Thermal resistance, corrosion resistance, coatability, thermal & electrical conductivity, magnetic properties, mechanical strength
Porous substruct. within foam	Micro porosity	Surface filtration, pressure drop

Table 2. Calculation of element composition of powder for a ferric alloy.

Composition [wt%]	Fe	Ni	Cr	Al
Alloy foam (FeNiCrAl)	22,40	49,60	22,00	6,00
Powder for alloying process	35,56	20,00	34,92	9,52

respect to the metal composition, because a wide variety of metal powders can be used (more than 40 different compositions were tested successfully). The high workability of the Ni foam allows it to be manufactured to the final geometry of the component after application of the coating, before the sintering stage. In this way complex components made of materials that are difficult to work are also easy to manufacture.

The powder composition has to be calculated such that the alloyed foam has the desired target composition. The amount of powder that has to be coated on the Ni foam was obtained by a number of coating tests. The percentage of powder with respect to the overall mass of the alloyed foam is called powder-foam ratio (PFR) and its optimum value is in the range of 59 ... 67%. In Table 2 the calculation is shown for a currently used alloy using a PFR of 63%. In terms of production capacity, upscaling has taken place: a pilot plant has been built near Munich with an output of about 100,000 m²/year.

3. Foam Properties

3.1. General Foam Properties

Properties will be summarized and discussed for one of the currently used FeNiCrAl alloys (composition see Table 2). The most important properties of the Ni and alloy foam, e.g. density and PFR, are summarized in Table 3. The density of the nickel foam increases by the powder coating process. The density of the alloyed foam is low with values between 0,41 and 0,72 g/cm³, which offers a high potential for lightweight metallic structures. Further foam properties are summarized

in Table 4. The bending properties were tested at room temperature. As there is a foam anisotropy in terms of mechanical properties, measurements were done along two of the representative foam directions designated longitudinal (L) and transverse (T). The anisotropy comes from the slight elongation of the pores during the Ni-foam production process.

3.2. Oxidation and Corrosion Resistance

An analysis of the behaviour of the foam after being exposed to high temperatures was carried out. In order to evaluate the oxidation resistance, the foam was exposed to air at set temperatures between 700 – 1000 °C for 20 h. After the tests, the mass gain, which is a value of the amount of oxidation, was measured and the material was analyzed by EDX.

Fig. 4 shows a mass gain comparison for different temperatures. Clearly the FeNiCrAl alloy is superior to Inconel 625 in terms of oxidation resistance. This is mainly due to its aluminium content, which enables the alloy to form an alumina layer and ensures a long-term oxidation resistance at temperatures > 950 °C.^[7,8] In this case chromium supports the alumina scale formation on the surface because it prevents the internal oxidation of aluminum.^[9] As it can be seen in Fig. 4, the amount of oxidation can be further reduced by pre-oxidizing this alloy, because the protective layer is then already formed before the foam is exposed to air at high temperatures (to be discussed in the subsequent section). The oxidation resistance of Inconel 625 is based on a chromia layer which is only stable for temperatures < 900 °C.

The mechanical behaviour after oxidation was also analyzed. This was done by 3-point bend testing (support width: 25 mm, crosshead speed: 2 mm/min). Results are summarized in Fig. 5 (bending strength) and Fig. 6 (bending elongation). The behaviour of oxidized foam with respect to pore size is the same as observed in as-sintered state (i.e. decrease of strength in increase of elongation). With respect to oxidation temperature, the foam strength is only slightly influenced by temperatures up to 900 °C, the largest decrease occurs in the L direction between 900 °C and 1000 °C. The

Table 3. Summary of foam density (Ni foam and alloyed foam) and PFR for four commercially available pore sizes.

Pore size [µm]	Ni foam			alloyed foam			
	density (g/m ²)	density (g/cm ³)	thickness (mm)	density (g/m ²)	density (g/cm ³)	thickness (mm)	powder/foam ratio [%]
450	420	0,26	1,60	1150	0,72	1,60	63
580	420	0,22	1,90	1150	0,60	1,90	63
800	460	0,18	2,50	1195	0,48	2,50	62
1200	500	0,17	3,00	1235	0,41	3,00	60

Table 4. Summary of further foam properties(*L = Longitudinal direction, i.e. the foam coiling direction; T = Transverse direction being perpendicular to L).

foam quality* / properties	D450	D580	D800	D1200
bending strength [MPa] L / T *	23,3 / 14,3	11,5 / 7,6	6 / 3,8	4,7 / 2,5
bending elongation [%] L / T *	4 / 6,0	4,6 / 6,9	7,7 / 10,3	7,7 / 14,6
specific surface area [mm ² /mm]	21	15	12,5	11
open porosity [%]	92	90,2	90,5	91,4
thermal conductivity [W/m*K]	0,228	0,209	0,224	0,21
CTE [1/K] 20 °C – 600 °C		0,000015		
heat capacity c _p [J/(g*K)] 100 – 500 °C		0,51 – 0,58		
melting range alloy foam [°C]		1320 – 1350		

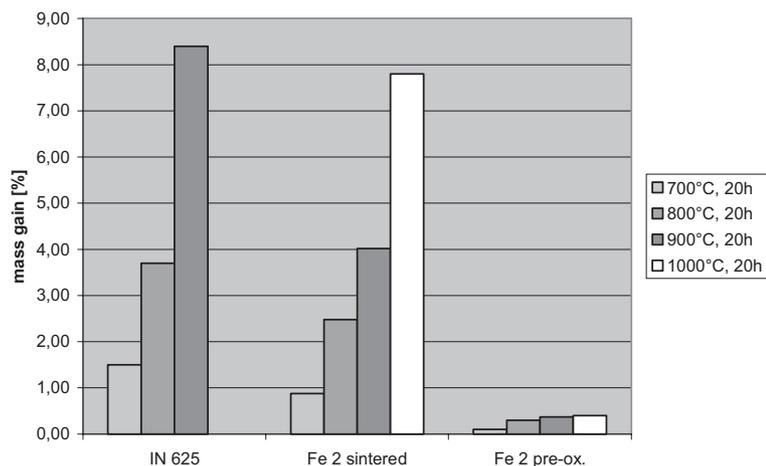


Fig. 4. Mass gain comparison after oxidation between Inconel®625 (IN 625) in sintered state and currently used FeNiCrAl alloy foam in sintered and pre-oxidized state (note: no value is given for IN 625 at 1000 °C, because the foam was completely oxidized).

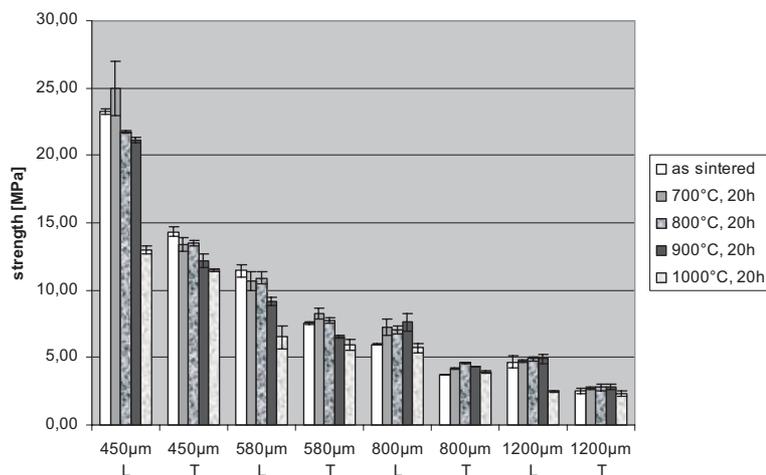


Fig. 5. Foam strength of FeNiCrAl alloy in oxidized state for different foam qualities.

bending elongation decreases by 30 – 50% with oxidation temperature; the largest gap is between the sintered state and the oxidation temperature of 700 °C. None of the samples appeared brittle after oxidation.

Another test, which the foams had to undergo, was a durability test under a diesel exhaust model atmosphere (gas composition: 12%CO₂, 10%H₂O, 6%O₂, 200 ppm SO₂, balance N₂) for 10, 30 and 100 h at 900 °C. In this test, a sintered sample was compared to two samples being pre-oxidized at air and low oxygen partial pressure (this regime will be explained in more detail within the next chapter). Results in terms of the mass gain are shown in Fig. 7. The following general conclusions can be drawn:

- the mass gain increases with time and temperature
- pre-oxidation helps to decrease the mass gain (i.e. due to passivation the amount of corrosion under diesel exhaust is reduced)
- the degree of improvement is different between the two regimes “air” and “low p(O₂)”; the latter leads to the formation of a more protective passivation layer

Within the respective regimes, the amount of oxidation can be further lowered by:

- increasing pre-oxidation temperature & time (air)
- decreasing oxygen partial pressure (low p(O₂))

3.3. Enhancing High-Temperature Stability by Pre-Oxidation

As the foams are exposed to high temperatures for longer service times, pre-oxidizing the foams in order to establish a protective layer helps to enhance corrosion resistance. The most desirable protective layer is α -alumina, as it has the best high-temperature protective characteristics. As the currently used FeNiCrAl alloy contains aluminium, it is expected to form an alumina layer in contact with oxygen. However, the formation of oxides other than alumina needs to be avoided, as they

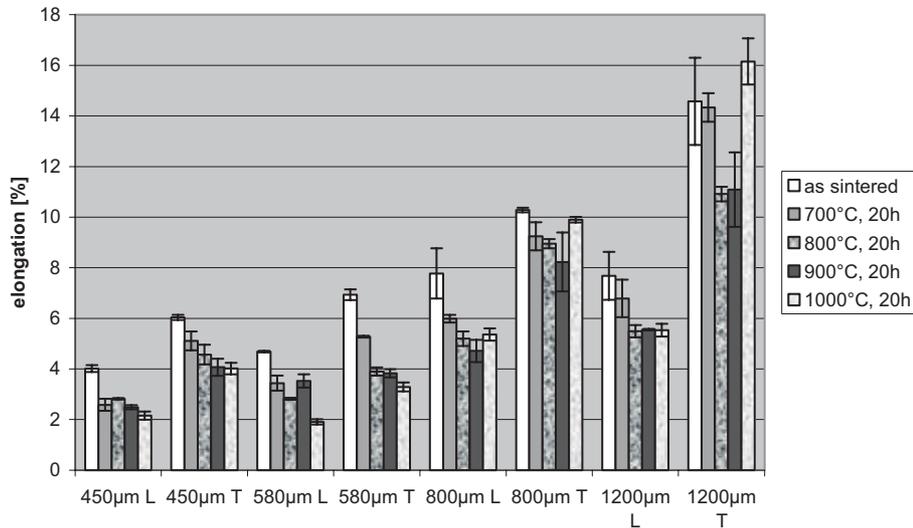


Fig. 6. Bending elongation of FeNiCrAl alloy in oxidized state for different foam qualities.

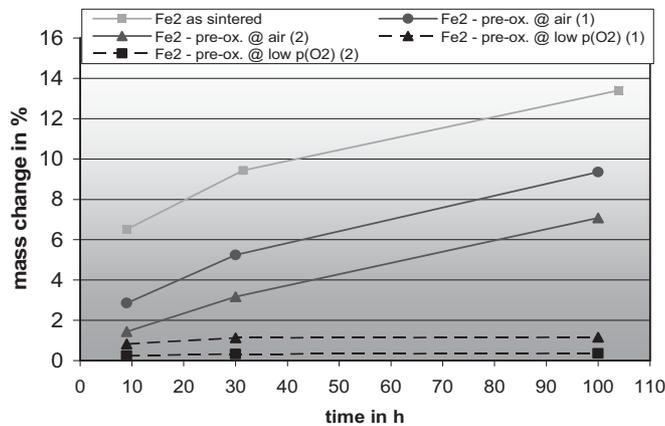


Fig. 7. Mass gains of sintered and pre-oxidized FeNiCrAl alloy under diesel exhaust atmosphere at 900 °C after 10, 30, 100 h (source: Dechema, Frankfurt).

may be harmful to layers, which are coated on the foam (e.g. catalytically active layers). In addition the oxidation resistance increases with the homogeneity of the alumina scale. A regime with an oxygen-containing atmosphere was found, which ensures the formation of only α -alumina.

Therefore it becomes necessary to adjust the oxygen partial pressure in the pre-oxidation atmosphere. To suppress the chromia formation, a partial pressure $p(\text{O}_2)$ has to be $< 10^{-18}$ bar while the alumina forms at $p(\text{O}_2) > 10^{-28}$ bar. The result of the optimized pre-oxidation conditions is a dense and homogeneous protective layer, without other oxides formed above it (as it also acts as a diffusion barrier). An example is shown in Fig. 8; only alumina is formed (in principle all other oxides, e.g. from Ni, Fe and Cr can also form, but are suppressed). As this sample has also been aged (1000 °C, 20 h, air), the suitability of the protective layer as diffusion barrier was also proven. The microstructure of the strut material shows no internal oxidation or AlN precipitates. Generally, without a dense alumina scale nitride forma-

tion is observed for commercially used alumina formers like FeCrAl and NiCrAl.^[10] In this case aluminium would be consumed near the surface which results in a weak alumina scale formation and a less oxidation resistance. Therefore the pre-oxidation conditions have an important effect on the high temperature performance of the foam material.

4. Applications

4.1. Overview

The unique combination of properties of the INCOFOAM[®] HighTemp allows it to be used for a wide variety of applications, which include:

- filtration at high temperatures (i.e. as diesel particulate filter (DPF) or diesel oxidation catalyst (DOC) in the exhaust stream of automobiles)
- noise absorber
- heat exchanger

Currently the focus is on the DPF application. Due to the good manufacturability of the foam and different available pore sizes, filtration properties can be tailored, e.g. by the design (Fig. 9) or by changing the pore size along the gas flow in order to adjust soot distribution, backpressure and filtration efficiency. Foam sheets can be joined by either coiling or by sintering them in stacks (Fig. 10). The foam sheets can be cut, stacked or rolled to the final axial (Fig. 10(a)) or radial (Fig. 10(b)) design. Fig. 10(c) shows an example for a canned radial filter. With regard to a low back pressure the radial filter design is preferred (Fig. 9(d, e), 10(b, c)). In order to increase conversion efficiencies at lower temperatures, catalytically active layers containing platinum ("washcoat") are coated on the alloyed foam (Fig. 11). The rough surface of the foam material ensures a very good adhesion of the wash coat.

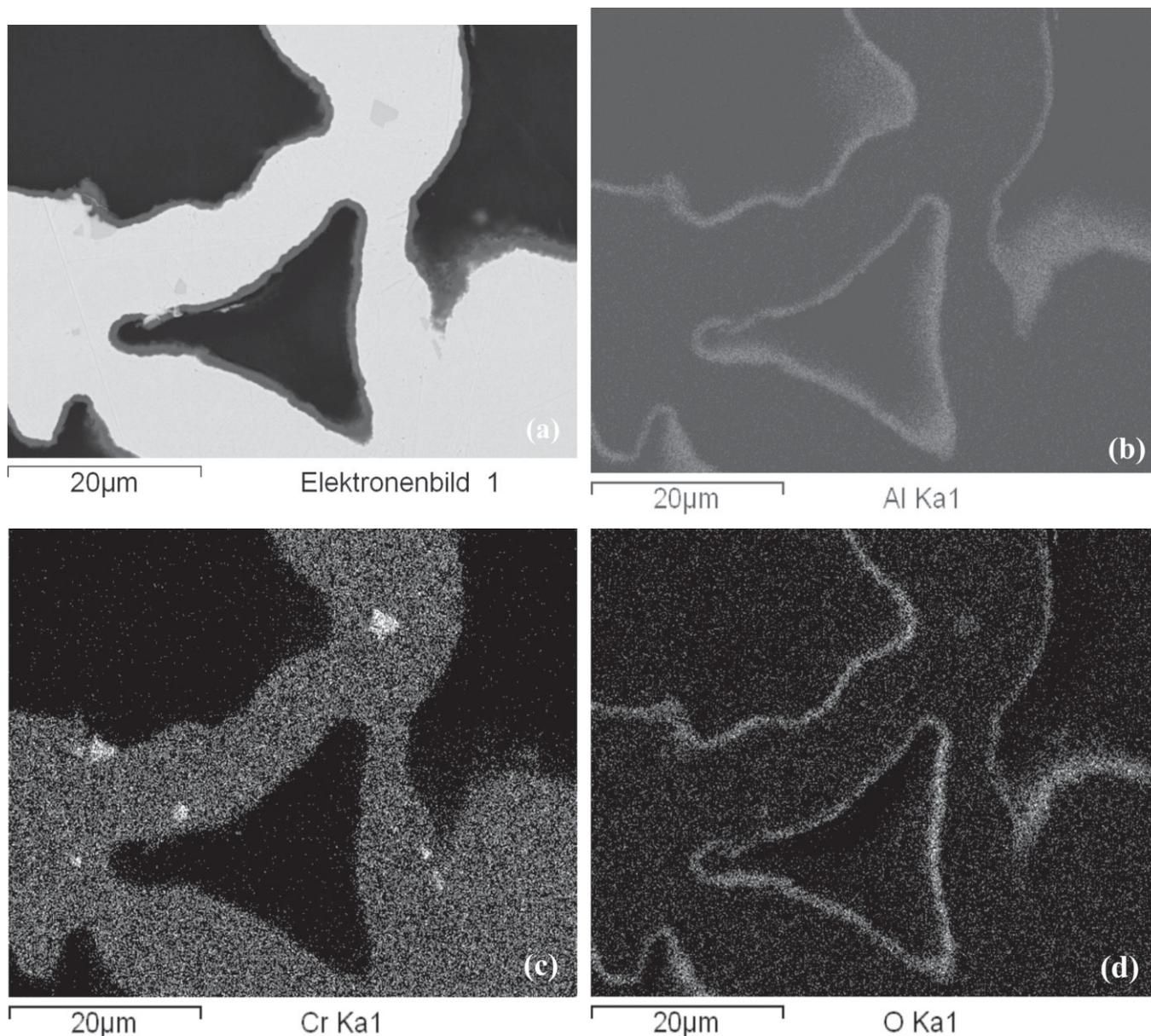


Fig. 8. Element distribution measured by EDX of pre-oxidized and enclosed at 1000 °C, 20 h under air aged sample: (a) BSE image, (b) aluminium, (c) chromium, (d) oxygen.

4.2. Filtration Data

Some selected results will be presented in this section and foam filters are compared vs. surface/wall-flow filters. More detailed test results are described in a separate paper.^[11,12] With surface filtration technology, the soot is collecting only on the strut surface of the foam, while the pores are not blocked (Fig. 12). Therefore the back pressure increase with high soot loading is limited. The same effect can be observed for ash accumulation. Wall-flow filters have a considerable loss of filtration volume over the filter lifetime because the pores are blocked by the accumulated ash; by comparison, the structure of the foam filter remains open for its lifetime. Compared to the state-of-the-art wall-flow filters, the regeneration of the deep-bed foam filters occurs faster and at low

temperatures because of improved soot contact. Furthermore no soot-blow off was observed under different conditions on bench and vehicle tests.

In Fig. 13 pressure drops are compared for different radial metal foam DPFs with ceramic DPFs (foam DPF volume: 2,5 l). The pressure drop occurs due to the loading of the filter with soot and therefore, it increases with soot loading. The 580 µm foam filter has a lower pressure drop than a comparable SiC filter and it can be decreased further by using foams of different pore sizes (labeled as "porosity gradient"). Therefore, in terms of pressure drop the metal foam filter can compete with currently used DPFs.

A further potential application is the diesel oxidation catalyst which is described in more detail in another work.^[12] Fig. 14 shows a comparison of a foam and cordierite DOC

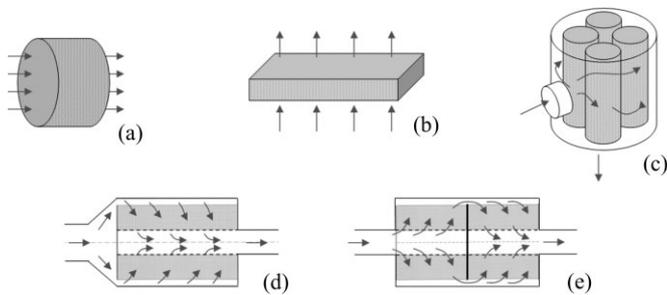


Fig. 9. Different designs for applications: (a), (b) axial flow filter, (c) parallel assembly of axial flow filters, (d) radial and (e) radial cross flow filter.

with respect to their hydrocarbon (HC) emission (cordierite volume: 1.25 l, foam volume: 0.36 l). Although the total Pt loading and volume of the foam DOC are smaller by a factor of 3.4, the total HC emission is comparable between the two DOCs, which is caused mainly by the higher surface and mass-transfer. Therefore, there is a great potential for component volume and Pt loading reduction, which in turn helps to reduce costs.

A summary of the main properties, which make the foam an attractive candidate for the DPF and DOC application, are summarized below:

- high design flexibility to meet the application requirements,
- low volume and weight,
- low heat capacity results in good cold start performance,
- faster regeneration at low temperatures because of improved soot contact by deep bed filtration,

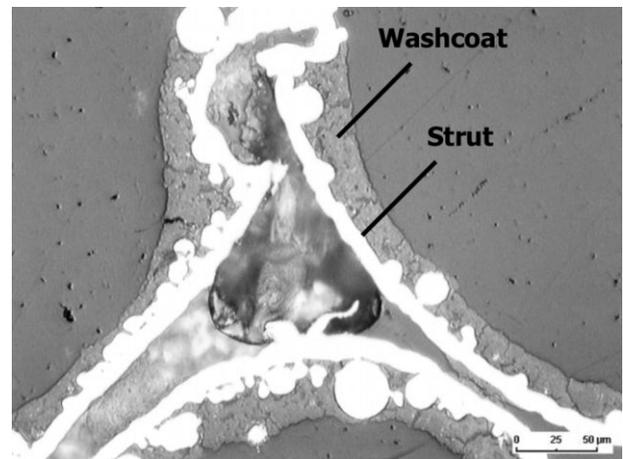


Fig. 11. Metallographical image of washcoated foam.

- high specific surface and therefore higher catalytic activity of the wash coat results in lower component volume and reduced platinum loadings which increases cost effectiveness,
- no pressure drop by ash accumulation over the life time.

5. Conclusions

A new powder metallurgical process was developed allowing the transformation of nickel foam into a high temperature corrosion resistant foam. This technology is cost efficient and suitable for a large scale production. Parameters such as

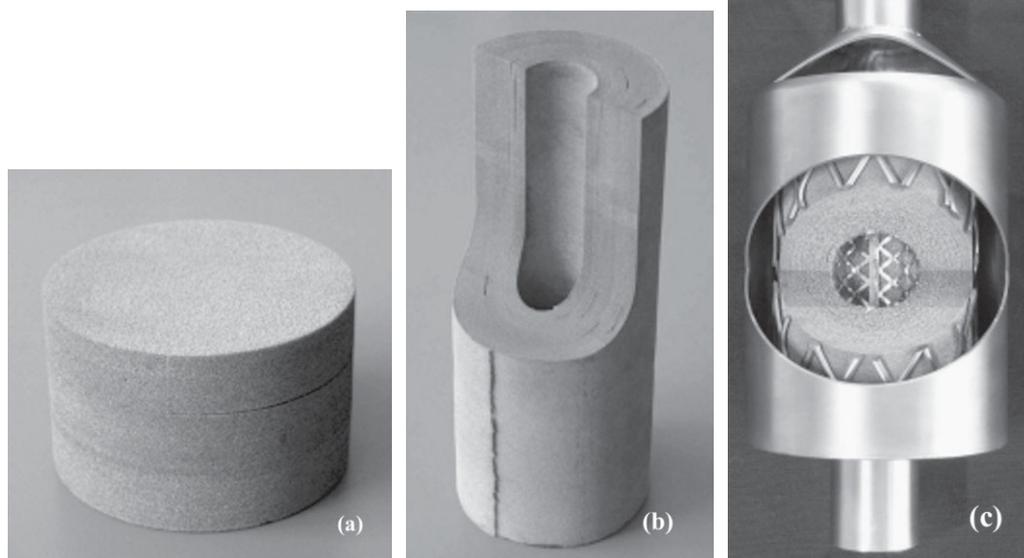


Fig. 10. (a) axial filter cut from sintered stack of foams, (b) radial filter made by coiling of foam sheets, (c) canned radial filter.

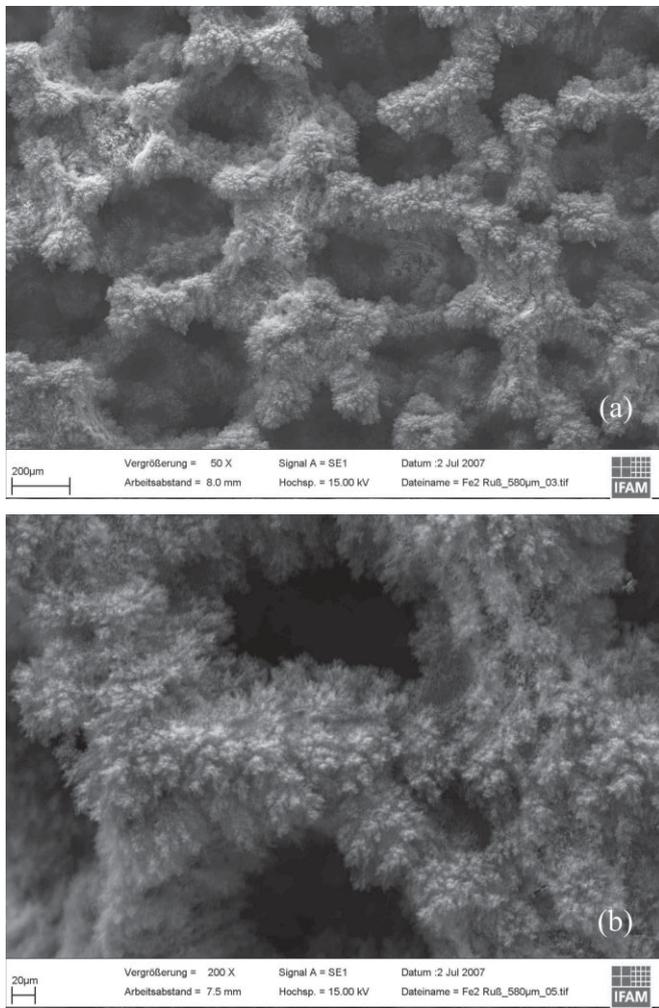


Fig. 12. SEM images of soot loaded foam (a) overview, (b) higher magnification, soot loading 9 g/l.

pore size and alloy composition can be varied in a wide range, and, combined with the good workability, make this foam especially promising in high temperature applications. High-temperature stability was described based on a FeNi-CrAl alloy, which shows very good results. Stability against corrosion at high temperatures can be achieved with this foam due to the fact that it establishes a protective layer consisting of α -alumina. With this foam, long term stability can be achieved for temperatures $> 950^\circ\text{C}$. Furthermore it was shown that pre-oxidizing the foam before putting it into service improves its already-high corrosion resistance. A pre-oxidation technology has been developed that ensures exclusive formation of α -alumina. In terms of high temperature applications, the foam is a possible candidate for filtration, heat exchangers and noise absorption. In the field of diesel particulate filters (DPF) and diesel oxidation catalysts (DOC) the new foam material offers a high soot filtration performance and a high effectivity as a catalyst carrier.

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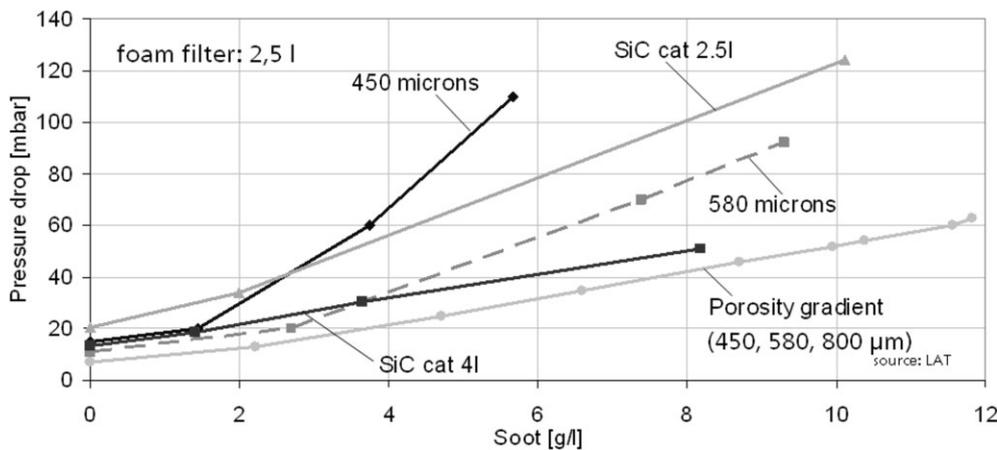


Fig. 13. Pressure drop vs. soot loading (engine speed: 1700 RPM) (source: LAT, Thessaloniki).

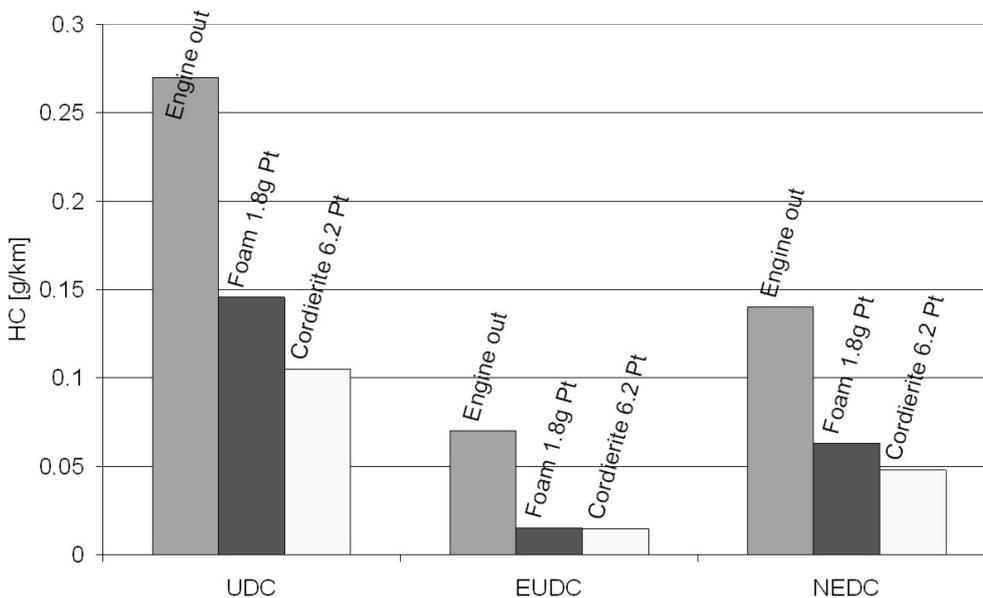


Fig. 14. Hydrocarbon emission under different driving cycles (UDC = urban driving cycle, EUDC = european driving cycle, NEDC = new european driving cycle), (source: LAT, Thessaloniki).

- [1] A. Böhm, H. Goehler; D. Naumann. *German patent, DE 101 50 948 C1, 2003.*
- [2] G. Walther, A. Böhm, Th. Weißgärber, H.-D. Böhm, B. Engelmann, D. Naumann. *German patent, DE 103 16 929 B3, 2005, European patent EP 1 620 370 B1, 2006.*
- [3] A. Böhm, G. Walther, D. Naumann, L. Timberg. *German patent, DE 10 2004 014 076 B3, 2005.*
- [4] A. Böhm, G. Walther, D. Naumann. *German Patent, DE 103 46 281 B4, 2006, World Patent, WO 2005/037467 A2, 2005.*
- [5] A. Böhm, G. Walther, D. Naumann, L. Timberg. *German patent, DE 10 2005 010 248 B4, 2006.*
- [6] A. Böhm, G. Walther, D. Naumann. *German patent, DE 10 2004 032 089 B3, 2005.*
- [7] R. Bürgel, "Handbook High Temp. Mater." Braunschweig/Wiesbaden, Vieweg & Sohn, 1998, 352–388.
- [8] J. Huang, H. Fang, X. Fu, F. Huang, H. Wan, Q. Zhang, S. Deng, J. Zu, *Oxid. of Met.* **2000**, 53, 273.
- [9] W. J. Quadackers, "Fundamentals of Oxid. of Alloys", DGM workshop, Research Centre Jülich, 2006.
- [10] B. A. Pint, J. R. Regina, K. Prüßner, L. D. Chitwood, K. B. Alexander, P. F. Tortorelli, "Effect of Environ. on the Oxid. of Ingot-Proc. Iron Aluminides", Elsevier, 2001.
- [11] G. C. Koltsakis, D. Katsaounis, Z. C. Samaras, D. Naumann, Sh. Saberi, A. Böhm, *SAE paper 2006-01-1524, 2006.*
- [12] G. C. Koltsakis, D. Katsaounis, I. Markomanolakis, Z. C. Samaras, D. Naumann, Sh. Saberi, A. Böhm. 2007. *SAE Trans: J. of Fuels and Lubricants (2007-01-0659), 2007.*