Functional ceramic coatings for cellular metals

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1 Introduction

Cellular metals such as metallic hollow spheres structures, singles hollow spheres and open celled metallic foams are lightweight, ductile materials with an enormous application potential. Coatings, to functionalise and protect the surfaces of the cellular metals offer many novel application areas for such materials.

Wet chemical processes to form ceramic or thermoset coatings on cellular metals are an alternative technique to the established PVD and CVD methods. The coatings were synthesised by Liquid Phase Deposition (LPD), such as dip- and spray coating, of the cellular structures with inorganic polymers or sol/gel - suspensions. This low cost method, well known from the lacquer technology, allows the coating of bigger parts with difficult geometry. Subsequent thermal treatment of the as coated materials provided coatings under good reproducible conditions [1 -3]. In principal, two different kinds of coatings can be obtained by this process: thin, dense thermoset or ceramic coatings or highly porous ceramic coatings.

Possible applications for such functionalised materials are:

- Oxidation and corrosion protection – functional coatings enable the application of these materials at elevated temperatures and under corrosive conditions.
- Catalysis - combined lightweight, ductile catalyst supports with highly porous coatings with high surface area and defined pore size.
- Adsorption - permeable high surface materials for gas drying and cleaning.
- Medical - permanent or degradable coatings for implants
- Biotechnology - immobilization of micro organism and enzymes.
- Chemical process engineering - highly porous coatings with defined pore size and form as micro rectors.

2 Coating technology

2.1 Materials

Open cell metal foams, metallic hollow spheres, sintered hollow sphere structures, metallic fibre structures, but also metallic sheets and profiles can be used as substrate structures for the functional coatings. Coating materials (Precursors) are inorganic polymers such as polysilazanes; polysiloxanes, polycarbosilanes or metal alkoxides $(M(OR)_{x},$ with M = Si, Al, Ti, Zr…) and bioglasses Usage of filler systems broaden the functionality of the coatings such as thermal expansion, hardness, electrical and thermal conductivity [4]. The filler system will be developed individual for each application.

2.2 Coating Process

In order to form the coatings a dip-coating process was applied. The substrates were dipped into the precursor suspension and removed with a constant velocity. The film thickness depends on the viscosity of the suspension and the removing velocity. Subsequent thermal treatment of the as coated materials in inert gas or air provided a thermoset or ceramic coating under good reproducible conditions. The general technological steps are illustrated in figure 1.

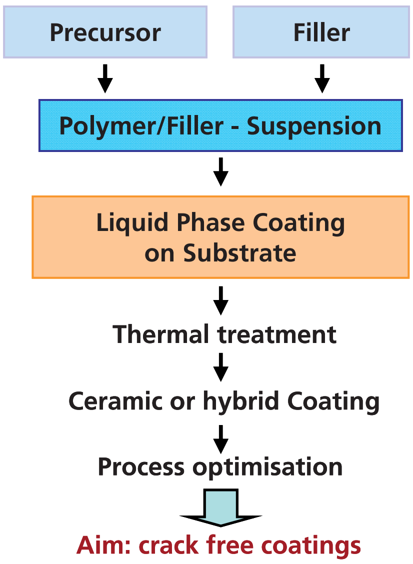

Figure 1: General technological steps of Liquid Phase Deposition (LPD).

3 Properties of the Coatings

3.1 General

In principal, two different kinds of coatings can be obtained by this process: thin, dense ceramic or hybrid organic-inorganic coatings or highly porous ceramic coatings with tuneable pore size, form and volume. The thickness varies from 100 nm to 200 µm and depends on the coating conditions. The results of GD-OES investigations prove diffusion of elements from the coating into the substrate during thermal treatment, this lead to the formation of an interface layer (see figure 2). The interface layer reduce the mismatch in the coefficient of thermal expansion of coating and substrate and allow direct chemical bonds between coating and substrate .This is the reason for the very good adhesion of the coatings in comparison to layers produced by physical methods. The coatings are high temperature stable and show a good oxidation and corrosion resistance.

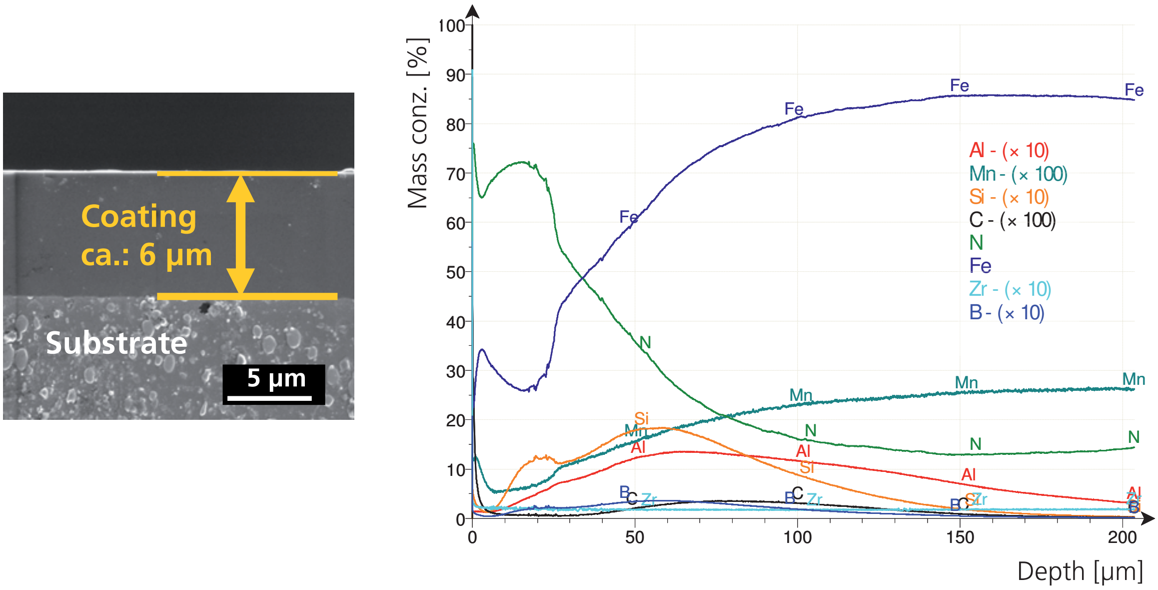

Figure 2: Micro structure of a polymer derived ceramic coating (left) and results of GD-OES investigations (right).

3.2 High porous coatings

Using sol/gel suspensions derived from metal alkoxides ($M(OR)_x$, with M = Si, Al, Ti, Zr…) and bioglasses lead to highly porous ceramic coatings. Pore size and specific surface area can be adjusted by insertion of organic spacer molecules, the film thickness and temperature and time of thermal treatment. Figure 3 show metallic hollow spheres (stainless steel 316L) coated with a bioglass. ($SiO_2/Ca_3(PO_4)_2$). A homogeneous and crack free coating was obtained with a thickness of 20 µm.

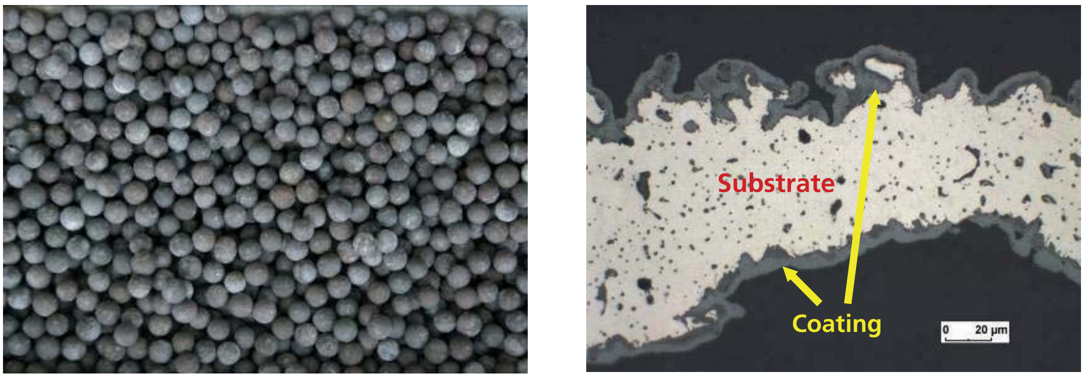

Figure 3: Metallic hollow spheres (stainless steel 316L) coated with a bioglass (left) ; cross section (right).

Annealing experiments of the coated hollow spheres show that best results concerning high specific surface area will be achieved by a thermal treatment of the samples at 600 °C in air (see Figure 4a). Low thickness of the coatings and the large differences in the density of coating and substrate materials complicate the correct measurement of the specific surface area. Figure 4b illustrate the results of the comparison of the calculation of the BET surface of porous Al_2O_3 and

ZrO2 coatings with and without consideration of the mass of the substrate (HS) after annealing at 800 °C. Without consideration of the mass of the substrate a BET surfaces of 5.24 m^2/g for Al_2O_3 and 2.58 m^2/g for ZrO_2 are obtained. This value is comparable with similar material for high temperature catalysis.

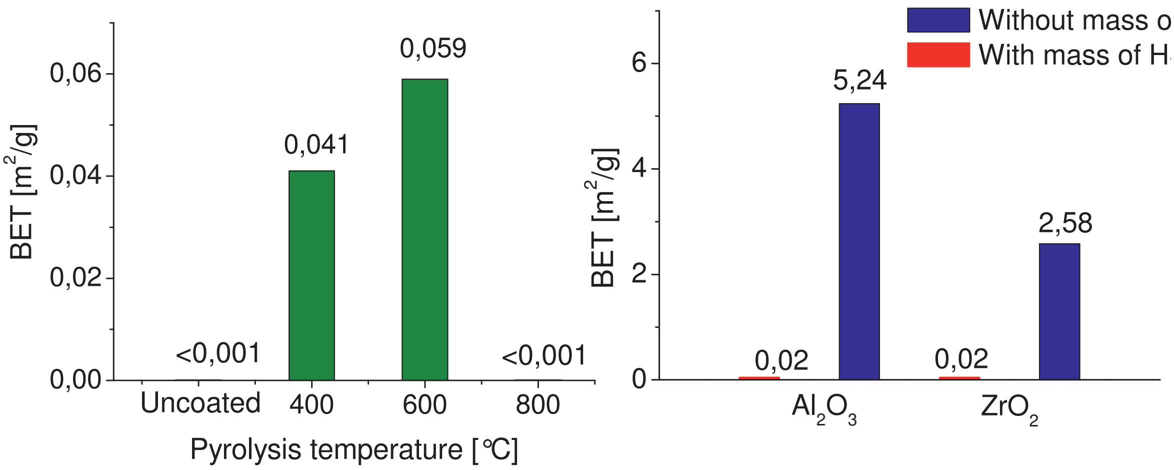

Figure 4: a): Temperature effect on BET surface for bioglass coatet metallic hollow spheres (316L); b): Comparison of the calculation of the BET surface of porous Al_2O_3 and ZrO_2 coatings with and without consideration of the mass of the substrate (HS) after annealing at 800 °C.

3.3 Dense coatings

One of the main applications of dense ceramic coatings is the protection of materials against oxidative attacks. This allow the extension of lifetime of materials under operation conditions or the usage of cheaper, lower alloyed steel. Figure 5 show an open celled metallic foam based on carbonyl iron coated with a filled ceramic SiCN coating. The coating is derived from a commercial polysilazane (HTT 1500, Clariant Advanced Materials, Germany). A homogeneous and dense coating with a thickness of approximately 20 µm was obtained.

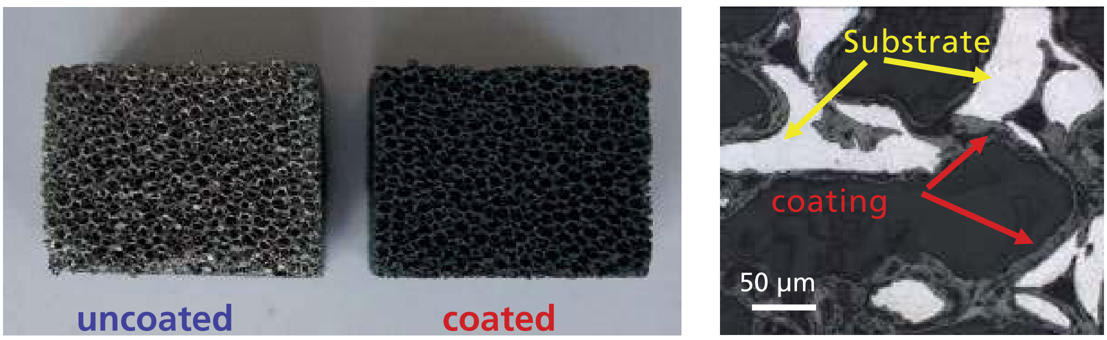

Figure 5: Open celled metallic foam based on carbonyl iron coated with a filled ceramic SiCN coating.(left); cross section (right).

Several filler systems based on Al_2O_3, SiO_2 and ZrO_2 were tested to improve the oxidation resistance of the coating material. As in figure 6 illustrated, Al_2O_3, SiO_2 and ZrO_2 filled SiCN coatings are good high temperature oxidation protection coatings with good thermal shock resistance. Coatings pass oxidation tests (50 h, 800°C, air) with oxidation rates up to 20 times lower than uncoated material. The best performance will be achieved by using ZrO_2 filled SiCN coatings (see Figure 6).

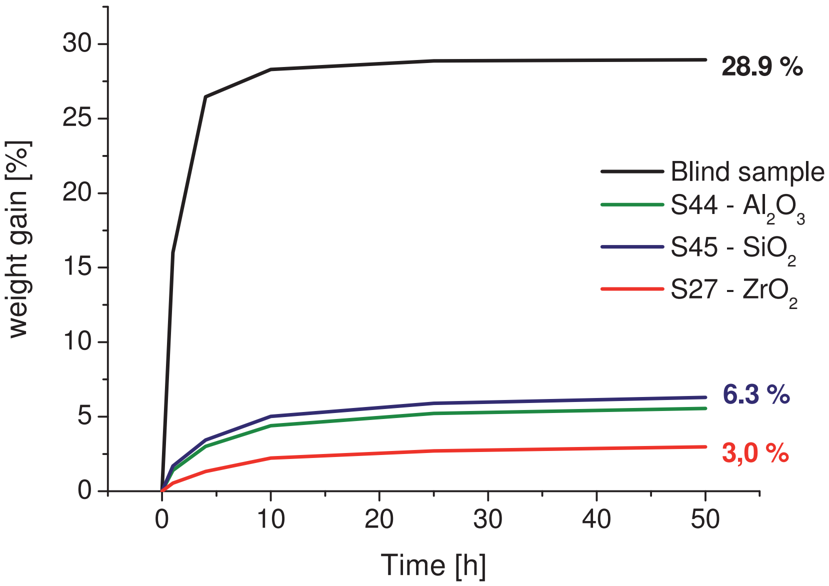

Figure 6: Results of Oxidation tests on open celled metallic foam based on carbonyl iron coated with a filled ceramic SiCN coating. (50 h, 800°C, air).

The sintered metallic hollow sphere structure based on stainless steel (FeCrAl) in figure 7 is coated with a pure SiCN coating derived from the polysilazane HTT 1500 (Clariant Advanced Materials, Germany). Because of the small cavities in between the hollow spheres a polymer solution with a very low viscosity was needed for a complete coating. For this reason it was not possible to use fillers, so the structure was coated with a pure polymer solution. The results of the oxidation test (400 h, 1100°C, air) evidence the SiCN coating with a thickness of 7 µm is sufficient for a good high temperature oxidation protection in comparison to the uncoated sample.

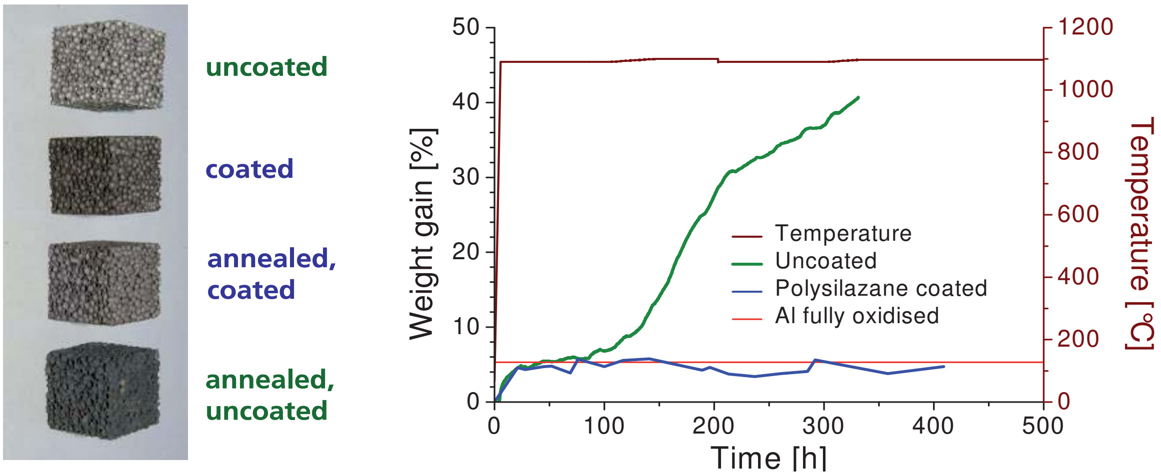

Figure 7: Sintered metallic hollow sphere structure based on stainless steel (FeCrAl, 1.4767) coated wit a pure ceramic SiCN coating (left); Results of the oxidation test (400 h, 1100 °C, air), (right).

4 Conclusion

LPD methods can be used to functionalise cellular metallic materials with thin, dense ceramic, hybrid organic-inorganic coatings or highly porous ceramic coatings. The broad field of applications of such functionalised cellular metallic materials comprised oxidation and corrosion protection, catalysis, adsorption materials, medical applications, and materials for the biotechnology and chemical process engineering.

5 References

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