

Chemical vapor deposition in spouted bed reactors.

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Chemical vapor deposition (CVD) on powders is often performed in a fluidized bed (FB) reactor. Following this technique, a bed of solid particles over a gas-distributor (called the grid) is made to behave like a liquid by passing gas through it at a flow rate included between two critical values. The gas contains the CVD precursors and the required activation energy for the deposition is most often provided by resistively heating the volume corresponding to the fluidized bed. The design of the grid is a hard point in such a process considering its plugging up with either powders or deposited solids. A radical solution to this problem is a reactor which does not contain any grid or other support to maintain the particles in the deposition zone.

In the present paper, the alternative to fluidized bed reactors for the CVD on powders, are first reviewed. These are rotating drum reactors, counter-current moving bed reactors, floating-type and fast circulating fluidized bed reactors, and finally spouted bed (SB) reactors. The selection of the type of the reactor depends on the constraints of the process, and especially on the characteristics of the powders to be treated, divided in four groups by means of the classical powder classification diagram by Geldart¹. Particular attention is paid to CVD processes performed in SB reactors, through a detailed literature survey. Such processes were first concerning coating of radioactive particles by pyrolytic carbon and silicon carbide for the preparation of high-temperature reactor fuel element spheres².

In a second part of the paper, results on SBCVD of Re and Ru on commercial NiCoCrAlYTa powders (Praxair, NI-482) used as bond coatings in thermal barriers for turbines will be presented. The aim is to investigate the influence of such a doping on the oxidation resistance of the bond coats. The determination of fluidization characteristics of these powders will be presented and compared with corresponding data of more classical powders. Then, results on the deposition of Re starting from rhenium carbonyl $\text{Re}_2(\text{CO})_{10}$ will be reported. There is actually no well established low temperature CVD route for the processing of metallic Re. Consequently, this new process required in a first step the determination of the vapor pressure and of the thermogravimetric characteristics of $\text{Re}_2(\text{CO})_{10}$. Figure 1 presents the vapor pressure of $\text{Re}_2(\text{CO})_{10}$ as a function of inverse temperature as was determined by a static method by using an isothermal chamber equipped with high-temperature Baratron gauges. $\text{Re}_2(\text{CO})_{10}$ can be sublimed without decomposition up to 120 °C where its vapor pressure is 139 Pa (1.04 Torr).

The low growth rate of Re deposited via pyrolytic dissociation of $\text{Re}_2(\text{CO})_{10}$ was revealed in preliminary runs on flat substrates and was confirmed from the deposition on the powders. Re-covered particles are shown in the SEM micrograph of Figure 2 and the Re coating is identified in the corresponding Re EDS

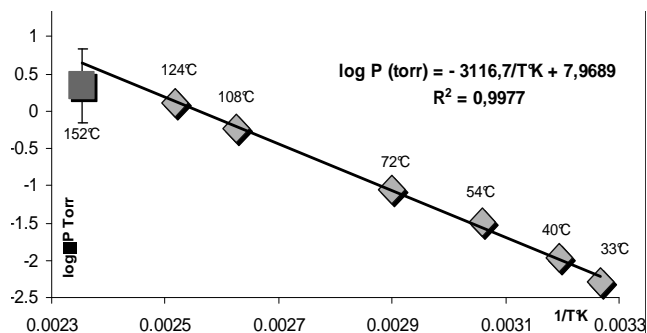


Figure 1. Vapor pressure of $\text{Re}_2(\text{CO})_{10}$ as a function of inverse temperature

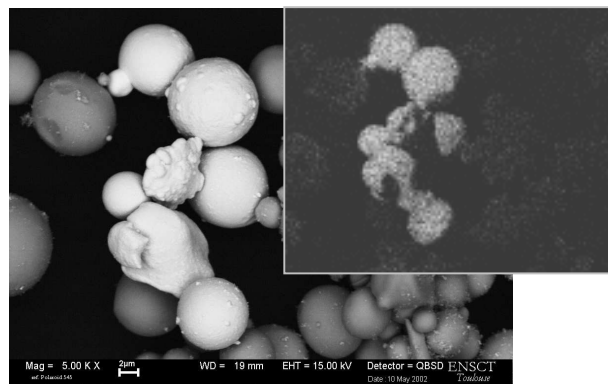


Figure 2. Secondary electrons SEM image of Ni-482 powders with Re deposited on their surface, and corresponding Re EDS map.

mapping shown in the insert micrograph.

Deposition of Ru was more successful, leading to the coverage of each NiCoCrAlYTa particle by Ru crystals with average size 100 nm in an one step process involving hydrogenation of the cyclopentadienyl ligands at 600 °C³. However, considerable carbon contamination was present in the deposits. An alternative route, involving O_2 instead of H_2 , yield ruthenium oxide, RuO_2 at 250 °C. In a second step, RuO_2 was reduced to carbon- and oxygen-free nanocrystalline Ru.

Finally, sintered doped and as-received NI-482 powders were subjected to isothermal and cyclic oxidation tests with the aim to compare their behavior in operating conditions corresponding to those of the MCrAlY bond coats during service.

This work demonstrated that the doping of commercial thermal barrier bond coatings in a laboratory scale in order to investigate the possible enhancement of their oxidation resistance is possible by a SBCVD process.

- (1) Geldart, D. *Powder Technol.* **1973**, 7, 285.
- (2) Heit, W.; Huschka, H.; Rind, W.; Kaiser, G. G. *Nucl. Technol.* **1985**, 69, 44.
- (3) Juarez, F.; Castillo, A.; Pieraggi, B.; Vahlas, C. *J. de Phys. IV* **2001**, 11, 1117.