

## New metal–ceramic composites grown by metalorganic chemical vapour deposition

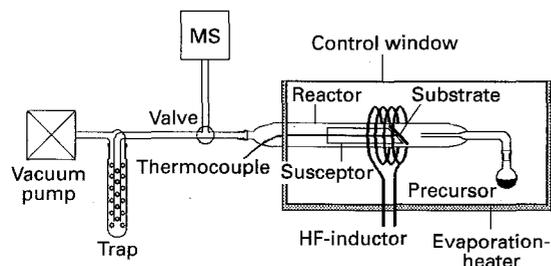
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While exploring new and effective routes to composites of ceramics and metals we have used the heterometallic alkoxide barium bis[*tert*-butoxystannate(II)],  $\text{BaSn}_2(\text{OtBu})_6$ , as molecular precursor in metalorganic chemical vapour deposition (MOCVD) techniques. The solid material obtained is characterized by highly dispersed metal in a ceramic matrix as determined by electron microscopy, electron spectroscopy and X-ray diffraction and therefore has peculiar chemical and physical properties. Furthermore the material is exclusively built of globular particles. In the one-component CVD process at low pressure heating is achieved by a microwave system.

To yield the new solid composite we have designed a CVD apparatus as shown in Fig. 1 which is especially useful for alkoxide precursors. The decomposition takes place in the temperature range 300–500 °C. This temperature is sufficient to decompose the precursor completely and is low enough to prevent carbide formation (the highest C-content found is 5% by photoelectron spectroscopy (XPS)).

The precursor barium bis[*tert*-butoxystannate (II)], obtained as described [1] and recrystallized from toluene, is incorporated into the system and the substrate is heated by induction to the temperature of decomposition which is 350 °C for  $\text{BaSn}_2(\text{OtBu})_6$ . The temperature of the outer furnace is successively raised until a continuous flow of precursor gas is reached which can be monitored by the unchanging mass spectrum of the reaction gases. If



**Figure 1** Schematic of the CVD equipment. It consists of a cylindrical reaction tube in which the substrate is situated on a glass support. The whole reactor is situated in a furnace, which is necessary to promote the volatility of the precursors at pressures of 0.1–1000 Pa. As substrates we are using nickel, graphite or silicon plates, but other materials are also possible. The substrate is heated inductively at temperatures of 300–500 °C. The temperature of the substrate is measured by a thermocouple and is connected to the high frequency source to monitor the temperature. The quadrupole mass spectrometer (MS) is linked to the system and enables control of the reaction gases.

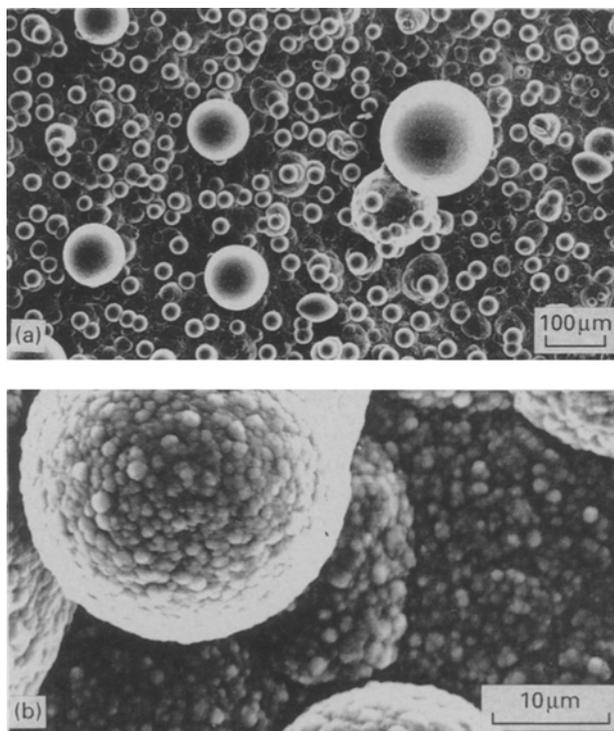
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all parameters (pressure, furnace temperature and substrate temperature) are well set, growing rates of 100  $\mu\text{m}/\text{h}$  of the composite can be achieved.

The analysis of the reaction gases during the thermolysis reveals *iso*-butene and *tert*-butanol as predominant gases. As further side components methane, acetone and dihydrogen can be identified, which are formed by a secondary reaction of the primary products.

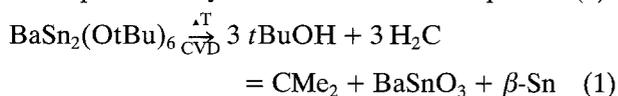
Electron microscopy studies of the produced solid material reveal a primary structure of ball-shaped particles which are composed of smaller globular particles (Fig. 2) in a secondary structure. The diameters of the primary balls are 20–200  $\mu\text{m}$  while the diameters of the secondary balls are about 200 nm. Energy dispersive X-ray analysis (EDX) reveals at this scale an homogeneous distribution of barium and tin at a molar ratio of 1:2 as in the starting molecule.

Using X-ray diffraction of the powdered compo-



**Figure 2** Representative scanning electron microscope (SEM) images of the metal–ceramic composite. Upper part: magnification 100, lower part: selected area of magnification factor 2000. Both pictures were obtained without sample treatment on a Jeol JXA 840 scanning electron microscope operating at 20 kV. The upper image shows the ball-like primary structure, while with the higher magnification (lower image) a second microstructure can be seen.

site, only  $\beta$ -Sn can be detected as crystalline component. When the sample is held several days at 500 °C crystallization of the former amorphous oxide part of the substance occurs and  $\text{BaSnO}_3$  (perovskite) may be recognized by its diffraction pattern. As can be deduced from these findings, during thermolysis of the precursor an electron transfer must have occurred. The two valent tins of the precursor molecule as diproportionating into Sn(0) and Sn(IV). The Sn(IV) together with barium is incorporated in an amorphous oxide. The whole CVD-process may be summarized as in equation (1).



Using scanning transmission electron microscopy (STEM) on powders of the composite which originate from squeezing, domains of metallic tin can be recognized together with domains of  $\text{BaSnO}_3$ , the largest homogeneous areas attaining 50 nm.

To further understand the construction of the balls making up the material the solid has been pressed into an indium foil and was shock frozen using liquid nitrogen. As a result the balls split into pieces. As can be deduced from scanning Auger electron microscopy studies the whole ball is built of a spherical nucleus which is surrounded by a shell very similar to a hazelnut (Fig. 3). Auger electron spectroscopy reveals the nucleus being made up exclusively of elemental tin while the shell is mostly formed of  $\text{BaSnO}_3$ , but also contains metallic tin. The diameter of the metallic nucleus and the thickness of the oxide shell are strongly dependent on such parameters of the CVD process as heating rate, pressure and substrate temperature. It can independently be shown by classical heating of the substrate that the ball-shaped manner of the composite is maintained, and is not a result of the microwave field.

The oxygen part of the sample has been found to be equal to 52 at % using XPS methods, which is near to the expected value of 50% for  $\text{BaSnO}_3^* \text{Sn}$ . The two different oxydation states of tin are nicely reflected by peak splitting of the corresponding binding energies (the  $3d_{5/2}$  peak is split into two

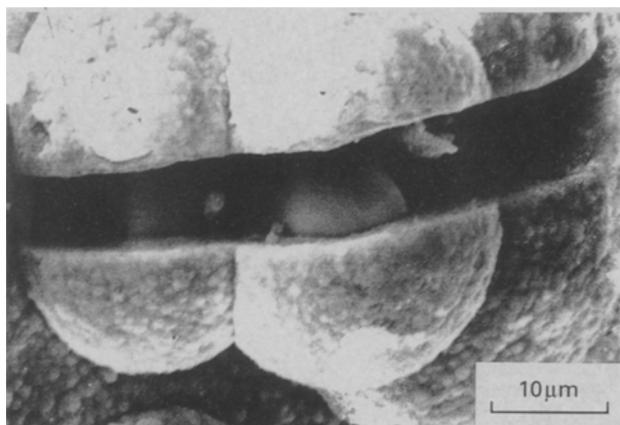


Figure 3 Scanning Auger microscope image of the obtained composite after freezing at  $-195$  °C. Some balls are broken in half so that the core, made up of  $\beta$ -Sn, can be seen inside.

peaks at 484.9 eV and 486.6 eV which is in perfect agreement for signals from  $\beta$ -Sn and Sn(IV) in an oxygen environment, respectively) [2]. The binding energy of the  $3d_{5/2}$ -signal of barium is found at 780.5 eV and corresponds to values found for Ba(II) in oxide compounds (779.65 eV) [2]).

No  $^{119}\text{Sn}$ -MAS solid NMR-spectrum of the composite could be obtained in accordance with signal broadening due to the weak paramagnetism of  $\beta$ -Sn present in the material and the  $5s^2$  electron pair (quick  $T_2$  relaxation).

As a consequence of the homogeneous distribution of the metal in the ceramic matrix the materials characterized have percolating properties and show conductivity (SIMIT effect) [3–6]. It may be used as a layer compound in electronics [7, 8] or as a cermet material [9, 10]. We have found that powders of the new composite can be easily pressed at ordinary temperatures to stable shapes. Our new vapour system allows one to produce layers of any desired thickness.

The fundamental new feature in the preparation of these composites is a chemical reaction which occurs between the linearly arranged metal atoms of the precursor molecule, and which dominates the decomposition process. As a consequence, a definite distribution of the metallic elements (Sn(0) on one side and Ba(II) and Sn(IV) on the other) over the whole substrate is achieved. At the hot surface, where the decomposition takes place, all components are unified at the shortest distance possible. So exact adjustment of the physical parameters of the process is not that important, as it is ‘chemistry’ which controls the decomposition.

The properties of our new nanocomposite can be altered over a wide range by using other precursors. The method described so far for  $\text{Ba}[\text{Sn}(\text{OtBu})_3]_2$  can be easily extended to other heterometal alkoxides (see patent), which may contain one or several low valent metallic elements [11–13].

### Acknowledgements and patent information

Instrumental support in scanning Auger microscopy and Auger electron spectroscopy by the Hoechst AG/Frankfurt (Dr C. Lang) is gratefully acknowledged. We would like to thank professor S. Hüfner and A. Jungmann (Universität des Saarlandes) for the photoelectron spectroscopic measurements, and M. Schuler (Universität des Saarlandes) for his assistance in electron microscopy. The obtained composites as well as the process of preparation have been deposited for patentation at the Bundesamt in Munich (Germany) [14].

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*Received 7 June  
and accepted 1 September 1993*