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GAS PHASE SYNTHESIS OF NANOSTRUCTURED FILMS AND COATINGS

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1. Introduction

Nanocrystalline materials have become increasingly important both in fundamental and applied research because of their interesting properties which are altered compared to conventional microstructures due to effects of grain size and due to the disordered atomic structure of the interfacial regions. For many years the research was concentrated on the synthesis and properties of nanocrystalline materials in bulk form which were prepared by consolidation and sintering of nanocrystalline powders prepared by wet chemical, gas phase and mechanical routes. Recently, as a response to the need of constantly improving the properties and performance of thin films and coatings, a potential for nanocrystalline materials in the area of novel synthesis and microstructures of films and coatings was identified. Many different techniques for the preparation of thin and thick films are readily available both for industrial applications and basic research and provide an excellent base for the development and application of new methods. The potential of nanocrystalline films and coatings can be identified in a wide range of technologies based on friction and wear properties, other mechanical properties such as superplasticity, and thermal conductivity for thermal barrier coatings, and optical, magnetic, electronic and catalytic properties.

In principle many different structures in thin films such as multilayers in electronic materials and for magneto-resistance effects (GMR, TMR etc.) should be included in a complete review of the topic of nanostructured films and coatings, because the characteristic dimensions are in the nanometer regime. However, it is beyond the scope of this paper to give a complete overview of all these structures and the corresponding processing techniques which are available for the synthesis of thin films and coatings. Therefore, the reader is referred to the literature on physical and chemical vapor processing techniques [1, 2]. Nevertheless, for the understanding of gas phase synthesis processes presented in the following sections it is worthwhile to note that the physical and chemical vapor deposition routes (PVD, CVD) have achieved a high degree of control and excellent reproducibility. Therefore, these techniques are widely spread in both research and production. The PVD and CVD techniques have capabilities to design materials at the atomic level by depositing atomic building units in a layer by layer growth to obtain atomically sharp interfaces between chemically or structurally dissimilar materials. In particular the design of semiconductor interfaces and magnetic multilayers has led to sophisticated artificial materials and unique applications associated with the well-defined nanostructures. As a disadvantage for production on a large scale, the processes for controlled growth are relatively slow.

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Additionally, the microstructures which can be obtained include single crystalline, epitaxial layers and columnar grain structures depending on the crystallographic relationships between the substrate and the growing film and the synthesis conditions (temperature, pressure, growth rate etc.). However, based on the knowledge of nanocrystalline materials in bulk form, it is anticipated that novel microstructures with grain sizes in the nanometer regime, controlled porosity with narrow size distributions and control of the chemical composition and the elemental distribution on the scale of the nanometer sized grains will open new areas of application. In this paper the opportunities for the growth of films and coatings with nanometer sized microstructures based on chemical vapor processing is reviewed.

2. The Chemical Vapor Synthesis Process

The process for film growth is based on the Chemical Vapor Synthesis (CVS) which has been described in detail in the literature [3]. The CVS technique itself is similar to the process of Chemical Vapor Deposition (CVD) which is widely employed to prepare thin films and coatings at a high level of control. The conditions for CVD growth have been determined for many materials systems and detailed knowledge exists for the dependence of the growth rate as a function of precursor partial pressure and temperature as well as other quantities influencing the growth of films on substrates. In the simplest form of a hot wall reactor the substrate is located in a cylindrical reactor tube heated with an external furnace. Other activation source such as microwave plasma can be employed as well. The complex growth process includes multiple steps such as decomposition of the metalorganic precursor molecules, gas diffusion to the hot substrate, deposition of the atomic species on the surface of the substrate and surface diffusion of the species to energetically favored sites on the surface such as steps and kinks. The growth rate of a film on a substrate depends on many parameter. It is shown schematically in Figure 1 as a function of the inverse temperature and the partial pressure of the precursor. Several distinct growth regimes can be identified in the dependence on the precursor pressure: (1) a regime in which the growth rate depends linearly on the precursor partial pressure; (2) a regime in which the growth rate on the substrate ceases to increase with increasing partial pressure and (3) a regime in which a rapid decrease at the highest partial pressures occurs. The best conditions for CVD growth are in the initial linear regime because the precursor decomposes and the reaction products are solely deposited at the surface of the growing films. Over a wide range of pressure no change in the mode of growth is observed and conditions for stable growth are given. In the plateau regime additional formation of nanoparticles occurs in the gas phase and consequently the growth rate of the film does not increase with increasing precursor partial pressure. At the highest partial pressures film growth is further suppressed and most of the precursor is transformed into nanoparticles because fewer precursor molecules reach the substrate surface. While this regime is not desirable in conventional film growth because of the incorporation of the nanoparticles into the films, this regime is used for the formation of nanoparticles by CVS. In this process the particles are collected from the gas phase after exiting from the hot wall reactor and can be processed further by consolidation and sintering.

The temperature dependence of the growth rate by CVD shows a similar behavior: (1) film growth occurs in the first two regimes with surface reaction control and gas diffusion control as rate determining steps. At higher temperatures the film growth rate decreases rapidly due to the homogeneous formation of nanoparticles in the gas phase. Therefore, optimum conditions for particle formation in the gas phase, i.e. CVS, require high temperatures and high precursor partial pressures.

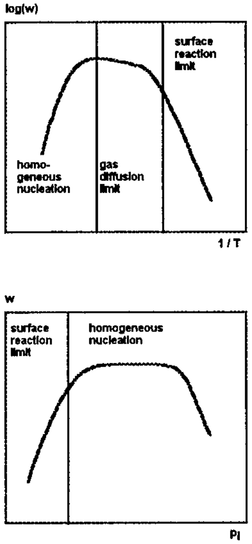

Figure 1: Schematic dependence of the film growth rate on a substrate by CVD growth as a function of the inverse temperature (top) and the precursor partial pressure P_i (bottom).

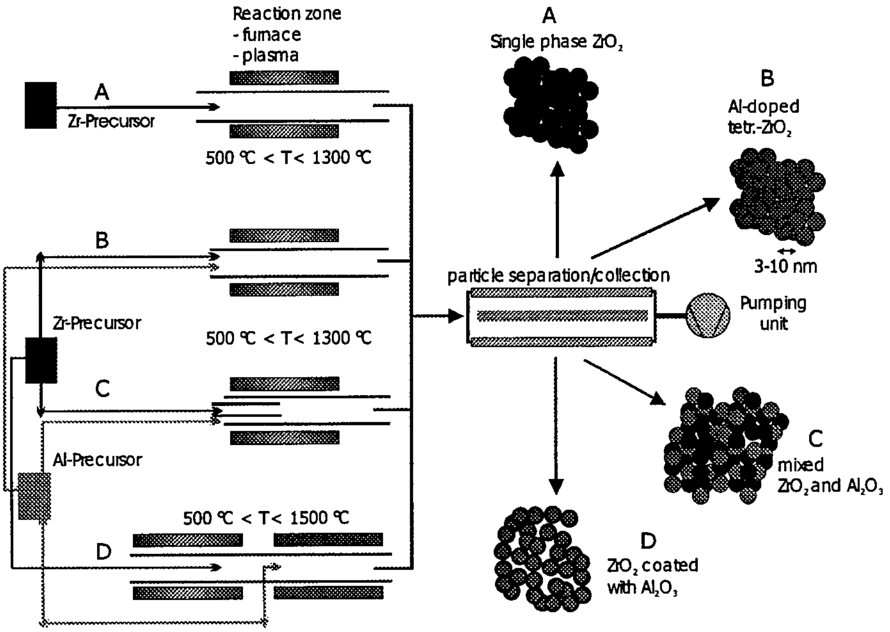

Figure 2: Opportunities of the CVS processing for the synthesis of nanocrystalline oxides with different elemental distributions of Zr- and Al-ions in the individual nanoparticles and the corresponding geometry of the various reactor designs.

The opportunities which result from the unique design of a hot wall CVS reactor for nanoparticle synthesis are illustrated schematically in Figure 2. The design is applicable in general for many materials systems, but as an example the consequences for the microstructure of the nanoparticles are shown for the ZrO_2/Al_2O_3 system, which is immiscible according to the equilibrium phase diagram. By changing the reactor geometry it is possible to synthesize oxide nanoparticles with different elemental distributions of the Zr- and Al-ions: crystalline and amorphous Al-doped zirconia, mixed pure oxides and coated nanoparticles. The possibility to control the elemental distributions within the nanoparticles opens many opportunities for the engineering of properties.

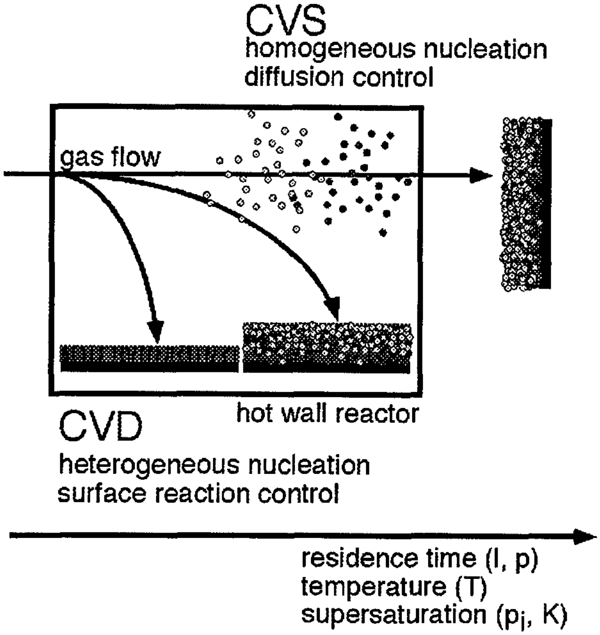

Figure 3: Various synthesis techniques based on chemical vapor processing: CVD for pure film growth with epitaxial or columnar grain structure, CVS for homogeneous formation of nanoparticles and CVD/CVS for nanoparticle deposition on a substrate with instantaneous sintering.

An interesting opportunity arises by the careful control of the synthesis parameter in the regime where CVD growth coincides with nanoparticle formation in the gas phase. At high precursor partial pressures and high temperatures, i.e. at high growth rates, it is possible to incorporate nanoparticles into the growing film, thus increasing the film growth rates compared to pure CVD growth. It has been demonstrated that nanoparticles which are formed in the gas phase can be deposited on the surface of a substrate held at high temperatures. Depending on the processing temperature it is possible to obtain porous or dense nanocrystalline coatings. The complete range of possibilities from epitaxial and columnar coatings grown by CVD, nanoparticles in the gas phase by CVS and the intermediate range of CVD/CVS as discussed above is summarized in Figure 3, highlighting the relationship between the different techniques. An important feature of the CVD/CVS regime is the high growth rate, because the total rate is determined by the sum of the film growth (CVD) and the nanoparticle deposition. In the parameter window of CVD/CVS growth rates exceeding those of CVD growth by far can be achieved. The general equipment for all three techniques is similar and includes the precursor sources, the hot wall reactor with a tubular reaction zone, process control equipment for pressure, temperature and mass flow and pumping. Depending on the precursor in use, the precursor delivery must be quite elaborate and consists of a bubbler arrangement for liquid precursors with high vapor pressures, mass flow controller for gaseous and volatile precursors or liquid precursor delivery systems exhibiting accurate delivery by precursor pumping and fast evaporation. As in CVD-processing extremely accurate control with reproducible parameters such as total and partial pressures, temperature, residence time, pumping speed, precursor and reactive gas flows etc. is possible and guarantees nanopowders and films of high quality. Further advantages of the CVS process compared to other gas condensation processing are better scalability, operator independent control of parameter, higher production rates (10 to 20 g/hr in a laboratory reactor).

3. Results

Different ceramics such as the simple oxides ZrO_2, Al_2O_3, Y_2O_3, TiO_2, doped oxides such as Y-ZrO_2 and Eu-Y_2O_3 and coated oxides nanoparticles such as ZrO_2 coated with Al_2O_3 and ZrO_2 coated with Y_2O_3 have been synthesized using the CVS process. It is important to note that the median and the width of the size distribution of nanopowders prepared by CVS is drastically improved compared to the values of powders prepared by Inert Gas Condensation (IGC) [4]. As can be seen in Figure 4, the particle size distributions of oxide nanopowders obtained by IGC have average particle sizes of approx. 10 nm and 8 nm for standard and optimum synthesis conditions, respectively, with a geometric standard deviation of approx. 1.8. The average particle sizes of CVS-powders are approx. 5 nm with σ=1.3. In combination with the reduced degree of agglomeration and the excellent cleanliness and crystallinity, the sintering behavior of the nanopowders are improved compared to IGC-powders, which have been shown to be improved compared to conventional powders. A sequence of samples in different stages of sintering shows that during the entire sintering process transparency is

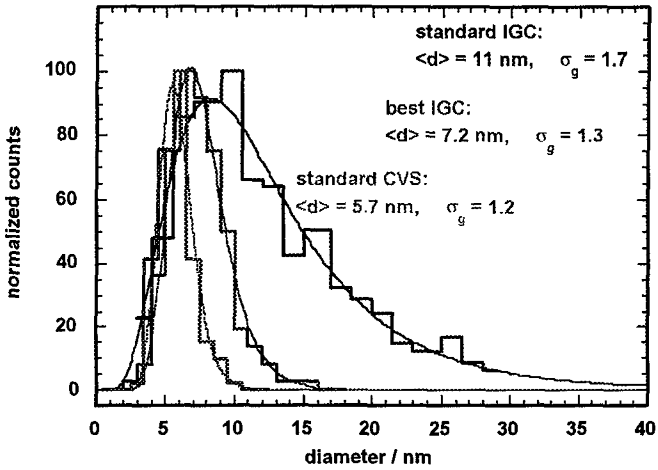

Figure 4: Particle size distributions for nanocrystalline ZrO_2 determined by TEM prepared by different gas phase routes: inert gas condensation (IGC) under standard and optimized (best) conditions and chemical vapor synthesis (CVS) under non-optimized conditions.

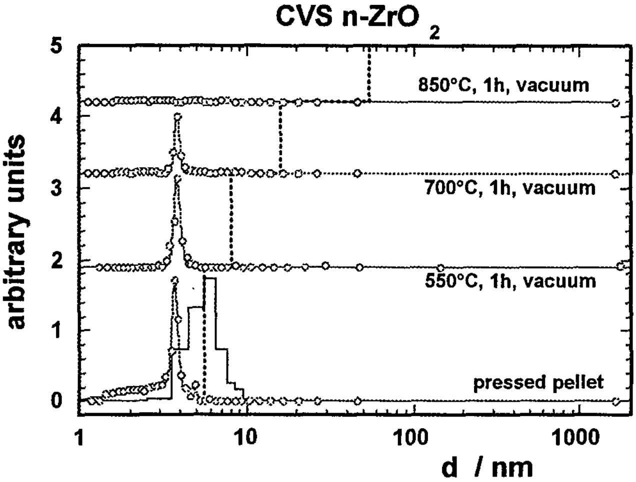

Figure 5: Pore size distributions of nanocrystalline ZrO_2 in the compacted state and after different sintering treatments determined by nitrogen adsorption. Included as dashed lines are also the average grain sizes at the different temperatures determined from the line broadening of XRD using the Scherrer formula. For the pressed pellet the grain size distribution determined by HRTEM is given as well.

maintained indicating that the pore size distributions are not changed significantly as has been observed in earlier sintering studies. Detailed analysis using nitrogen adsorption confirms this result as can be seen in Figure 5 for the pore size distribution of pure nanocrystalline zirconia obtained by BET/BJH analysis. The microstructural features, i.e. average particle size, size distribution, agglomeration, crystallinity etc., which have been described above for pure oxides can be maintained in the doped, mixed and coated nanoparticles as well. As an example, Figure 6 shows a high resolution transmission electron micrograph of Al_2O_3-coated ZrO_2 nanoparticles prepared by sequential deposition as described above (see Figure 2). The crystalline core of a ZrO_2-nanoparticle with a Al-rich amorphous coating layer can be clearly identified in the micrograph. The existence of a coating layer has also been demonstrated using EXAFS analysis with Reverse Monte Carlo (RMC) data evaluation, as described by Winterer [5]. It could be shown that depending on the processing conditions, a thin layer of Y_2O_3 on ZrO_2 nanoparticles can be obtained [6]. Even though the two precursors were introduced simultaneously into the reactor the slower decomposition kinetics of the Y-precursor resulted in a sequential deposition and formation of a coating on the ZrO_2 nanoparticles.

One of the main challenges during sintering of nanopowders is the prevention/suppression of grain growth during the high temperature processing necessary to obtain high densities. Due to the large fraction of interfaces, both the driving forces for grain growth and sintering are large. Consequently, during pressureless sintering the average grain sizes grow to the µm regime during the final stages of sintering. Different techniques such as pressure assisted sintering, hot-isostatic pressing and creep deformation have been employed to densify nanocrystalline oxides while minimizing grain growth. An interesting effect has been observed if a structural phase transformation under high pressure occurs at the sintering temperature. In this case which was observed for nanocrystalline TiO_2, a smaller grain size in

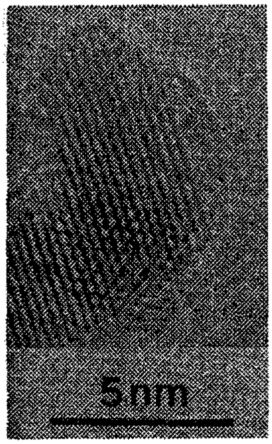

Figure 6: High resolution transmission electron micrograph of a ZrO_2 nanoparticle coated with a layer of Al_2O_3 prepared by CVS. (HRTEM: Courtesy of Dr. Miehe, Structural Analysis Division at Materials Science Department of Darmstadt University of Technology).

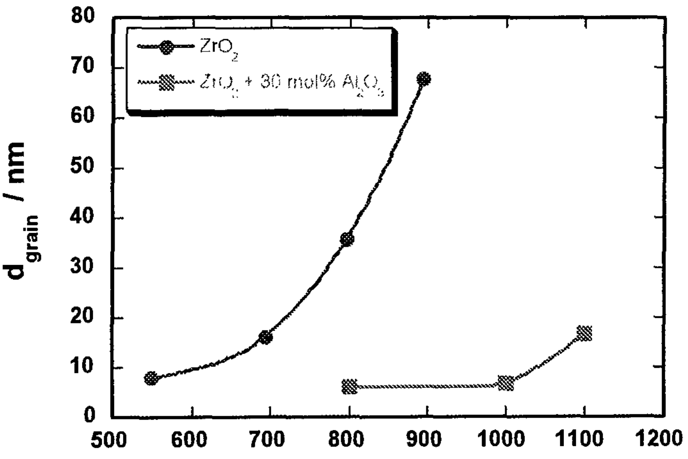

Figure 7: Grain size of pure nanocrystalline ZrO_2 and ZrO_2 doped with 30 mol% Al_2O_3 prepared by CVS. The grain growth can be suppressed effectively by the doping and grain sizes in the range of 20 nm can be stabilized even at temperatures of 1100 °C.

the dense ceramic than the original grain size in the powder was obtained due to a high nucleation density [7]. However, due to the high cost of pressure assisted sintering equipment, restrictions of sample size and time constraints, pressureless sintering is favorable. Consequently, grain growth has to be inhibited by other means, such as grain boundary segregation and addition of second phase nanoparticles with low solubility in the matrix. Both methods have been employed for various material systems and are based on the reduction of grain boundary mobility. It has been demonstrated that a crystalline ZrO_2 ceramic doped with up to 10 mol% Al_2O_3 can be sintered to theoretical density at 1100 °C with grain sizes below 40 nm, while a ZrO_2 ceramic doped with more than 15 mol% Al_2O_3 sintered to only 75 % density with grain sizes below 20 nm [8]. The results of these studies are summarized in Figure 7. The pore structure consisting of nanopores with average pore diameter below 10 nm was stable at sintering temperatures of 1100 °C. It should be mentioned that both microstructures, i.e. dense ceramics with nanometer sized grains and ceramics with a porosity in the nanometer regime, which are stable at high temperatures are of interest for advanced applications. Further investigations with mixed and coated nanoparticles are in progress.

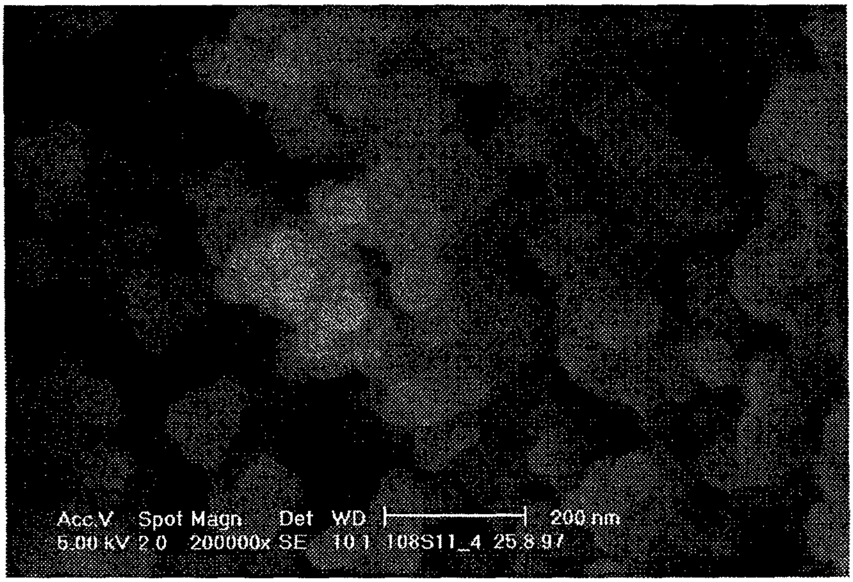

Figure 8: Backscattering image of the cross section through a Si-C-B gradient on a silicon substrate; position along the reactor axis 150 mm.

In relation to the synthesis of nanocrystalline films and coatings it is important that the microstructural features which are relevant for the sintering behavior of consolidated nanopowders also facilitate the densification of nanoparticles deposited on the surface of substrates during CVD/CVS processing. Similar to the results on bulk ceramics it has been shown that fully dense coatings can be readily obtained at sintering temperatures below 0.4 T_M. Additionally, the exact control of the precursor fluxes into the reactor, i.e. by adjusting the mass flow rates of precursors and reacting gases and composition of the precursors, allows a change of the growth mode. Similarly, a temperature ramp during deposition results in a change of the growth mode from pure CVD film growth to CVS nanoparticle deposition as indicated in Figure 1. As a consequence of the change of the growth mode the grain morphology changes from a columnar grain structure with intergranular porosity to a porous or dense nanocrystalline microstructure. Furthermore, employing this principle a gradient

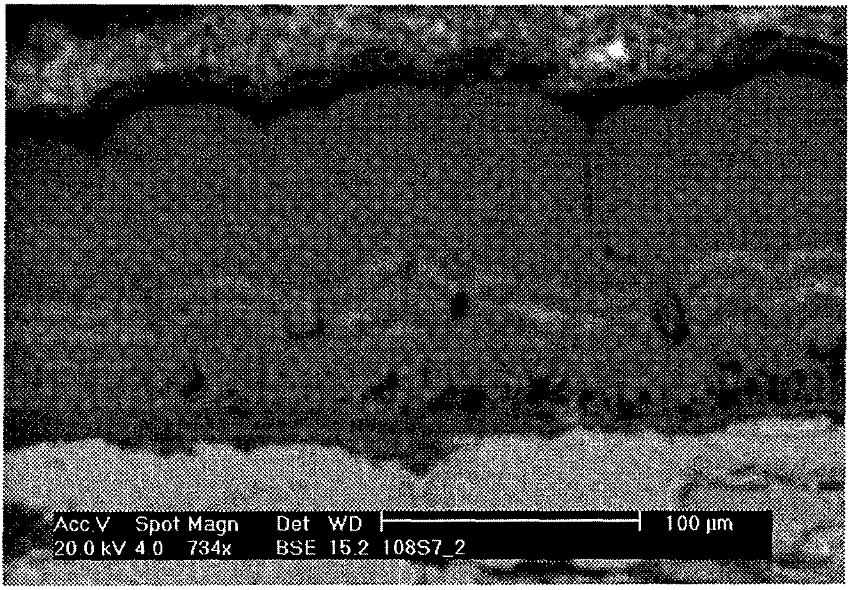

Figure 9: Transmission electron micrograph of the cross section close to the interface between the Si-C-B gradient film and the silicon substrate; position along the reactor axis: 250 mm.

structure with different grain morphologies was obtained for TiO_2 by changing the temperature profile continuously during deposition. Similarly, the composition can be changed by adjusting the flow rates of two different precursors during the deposition at constant temperature. The step-like gradient shown in the scanning electron micrograph of Figure 8 results from the distinct changes of the flow rates. However, with computer controlled equipment it is possible to design continuous linear compositional gradients across the thickness of the coatings. The high resolution scanning electron micrograph of Figure 9 shows clearly the nanocrystalline grains in the coating. The exact growth mode of the nanocrystalline coating is not yet established and it is not clear where the nanoparticles are formed. The size of the particles formed in the gas phase (by CVS) and the grain size in the coatings are similar which indicates that the nanoparticles are formed in the gas phase and are subsequently deposited onto the substrate. Since the deposition temperatures are high, appropriate means to suppress grain growth as discussed have to be taken to ensure the deposition of a nanocrystalline coating.

4. Acknowledgements

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