ON THE CHEMICAL VAPOUR DEPOSITION OF ZIRCONIA FROM $ZrCl_4-H_2-CO_2-Ar$ GAS MIXTURE: II. AN EXPERIMENTAL APPROACH

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Summary

Chemical vapour deposition (CVD) of zirconia, from a $ZrCl_4-H_2-CO_2$ -Ar gas mixture, has been studied experimentally.

On the basis of a kinetic approach, the deposition process is shown to be governed by chemical reactions (probably water formation) with an apparent activation energy of about 100 kcal mol^{-1} . With an increase in the total gas flow rate and the total pressure, the occurrence of an important homogeneous nucleation in the gas phase ("soot" formation) cannot be prevented.

The deposited zirconia films are found to be polycrystalline. A structural analysis by X-ray diffraction shows the possibility of depositing both monoclinic and tetragonal modifications of zirconia; such a mixture remaining stable down to room temperature. By Raman spectroscopic analysis, a small amount of weakly graphitized free carbon can be detected in the deposited films, depending on the deposition parameters. The stabilization of the tetragonal phase, at room temperature, can be explained on the basis of the effect of grain size, which has been thermodynamically studied by Lange *et al.*

1. Introduction

Compared with the chemical vapour deposition (CVD) of alumina from an $AlCl_3-H_2-CO_2$ system [1-4] the deposition process of zirconia from a $ZrCl_4-H_2-CO_2$ gas mixture, whose advantages have been previously discussed [5], has not been described, as yet, in much detail. Whereas a lot of articles have been devoted to the properties of sintered zirconia (particularly stabilized or partially stabilized zirconia) [6], very few studies have been concerned with the physical and chemical characteristics of CVD zirconia thin films prepared by hydrolysis of zirconium chloride [7]. The only contribution, to our knowledge, in this field is that of Brennfleck *et al.* [8] who asserts, through a kinetic study of the deposition process as a function of temperature and total pressure, that the formation of water $(CO_2 + H_2 \implies CO + H_2O)$ is the rate-controlling step of the overall reaction process. Their characterization of the so-prepared ZrO_2 thin films is limited to a morphological analysis carried out by scanning electron microscopy (SEM).

The present experimental study gives, on the basis of a specific deposition apparatus, an extended investigation of the influence of the deposition parameters on the growth rate and the physicochemical properties of ZrO_2 deposited on flat alumina substrates (Degussa-France: Degussit AL 23). Composition, structure and morphology of the deposits have been studied in more detail to establish some correlations with the deposition parameters.

2. Experimental arrangement

Zirconia deposition experiments were performed using a CVD apparatus with a hot-wall reactor working under reduced pressure (see Fig. 1).

The initial gaseous mixture contained the following: (i) CO_2 and H_2 used to form H_2O , (ii) Cl_2 used to prepare $ZrCl_4$ by passing across a small specific chamber containing zirconium sponge and heated to about 300 °C,



Fig. 1. Schematic diagram of the experimental apparatus used for ZrO_2 chemical deposition: 1, shut-off valve; 2, P_2O_5 purification; 3, manometer; 4, mass flowmeter; 5, flowmeter; 6, adjusting valve; 7, security valve; 8, chlorinator; 9, heating furnace; 10, CVD reactor; 11, water cooling; 12, thermocouple; 13, liquid nitrogen trap; 14, pressure sensor; 15, adjusting valve; 16, chlorinator temperature controller; 17, (Cl₂, CO₂, H₂) flow controller; 18, CVD reactor temperature controller; 19, pressure controller; 20, vacuum pump.

as well as eventually (iii) argon. The various gas flow rates and consequently the composition of the gas phase were controlled by means of mass flowmeters. The deposition chamber, made of alloys with high mechanical and chemical resistance, was heated resistively (up to about 1000 °C) by electrical resistances embedded in a thermal insulator. The size of the isothermal hot zone was 60 mm in diameter and 50 mm in height. The gaseous mixture produced by the CVD reactions was classically condensed in liquid nitrogen traps. In the reactor, a vacuum pump maintained a reduced pressure (down to about 1 kPa) whose value could be regulated electronically.

3. Experimental deposition rate of zirconia

Before examining the characteristics of the deposited thin films, a short kinetic study was performed as a function of total flow rate, temperature and total pressure, for a ratio $\alpha([H_2]/[CO_2]) = 1$.

3.1. Influence of the total gas flow rate

The deposition rate of ZrO_2 is plotted in Fig. 2 as a function of the total gas flow rate for a total pressure of 4 kPa and a temperature of 965 °C. A rapid increase is observed between 250 and 400 cm³ min⁻¹ and then the deposition rate does not seem to increase any further. Moreover, for higher gas flow rates (D > 500 cm³ min⁻¹), an important homogeneous nucleation occurs in the gas phase (soot formation), which results in very poorly adherent deposits and consequently decreases the growth rate of the deposit on the substrate.

3.2. Influence of the temperature

The variation in zirconia deposition rate vs. reciprocal temperature (semilogarithmic scale) are reported in Fig. 3 for a total gas flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$ and a total pressure of 2 kPa. The temperature range is limited to 800 - 1000 °C. At temperatures lower than 900 °C, the deposition rate



Fig. 2. Influence of the total gas flow rate on the zirconia deposition rate.



Fig. 3. Variation in the logarithm of the zirconia deposition rate with reciprocal temperature.

Fig. 4. Influence of the total pressure on the zirconia deposition rate.

is very low and the measurement not very accurate. Between 900 and 1000 °C, the variation seems to follow an exponential Arrhenius law, with a very high apparent activation energy of about 100 kcal mol^{-1} .

3.3. Influence of the total pressure

The deposition rate of zirconia is plotted in Fig. 4 as a function of the total pressure (in the range 2 - 10 kPa) for a temperature of 965 °C and two values of the total gas flow rate: 300 and 420 cm³ min⁻¹. A marked maximum is observed in both cases, for 3 kPa at 300 cm³ min⁻¹ and for 4 kPa at 420 cm³ min⁻¹. At pressures higher than 6 kPa the growth rate seems to become almost constant (about 0.5 mg h⁻¹ cm⁻²). In this relatively high pressure range an important homogeneous nucleation phenomenon occurs, which makes an accurate measurement of the deposition rate difficult.

3.4. Discussion

The very high activation energy is probably a consequence of a deposition process kinetically controlled by chemical reactions. This value is not far from the one estimated by Brennfleck *et al.* [8] (*i.e.* 86 kcal mol⁻¹) between 860 and 900 °C. On the basis of the high activation energy (78 kcal mol⁻¹) reported by Tingey for the homogeneous reaction of CO₂ with H₂ to form CO and H₂O at temperatures higher than 800 °C [9], this reaction of water formation can be assumed to be the kinetic controlling step of the overall deposition process. A further kinetic investigation, *e.g.* as a function of the H₂ and CO₂ concentrations, giving reaction orders with respect to these species, should be very useful to confirm the hypothesis and to approach more accurately the reaction mechanism. Moreover, the present experimental result does not reveal, up to 1000 °C, the transition (usually observed in CVD) towards a deposition process kinetically limited by diffusion of gaseous species through the boundary layer.

As a consequence, at a temperature of 965 °C and a total gas flow rate of about 300 cm³ min⁻¹, *i.e.* with a deposition mechanism governed by chemical reaction kinetics, the increase in the growth rate with increasing total flow rate can be explained by a supersaturation increase at the gas/substrate interface. For a total gas flow rate lower than 400 cm³ min⁻¹, the depletion of the gas phase (owing to, for instance, unwanted deposits on the hot walls of the reactor) is probably less and less important while the total gas flow rate is increased, as was previously found by Hannache *et al.* for boron carbide CVD [10]. At a sufficiently high gas flow rate (*i.e.* D > 400cm³ min⁻¹), the amount of gaseous reactants consumed by ZrO₂ deposition on the reactor walls becomes negligible with respect to that flowing at the gas inlet; the supersaturation at the gas/substrate interface does not vary significantly any longer and the deposition rate becomes almost constant.

4. Physicochemical properties of CVD zirconia thin films

The investigation of Brennfleck *et al.* in this field was limited to some morphological observations by SEM [8]. These workers did not characterize their CVD zirconia thin films from a chemical and structural point of view. The present paper reports the influence of the experimental parameters particularly on the occurrence of carbon in the deposited films and the transition between the various phases (especially the monoclinic \rightleftharpoons tetragonal phases).

4.1. Morphological analysis of zirconia deposits

The SEM micrographs presented in Fig. 5 illustrate the influence of deposition temperature (in the range 800 - 1000 °C) on the morphology of zirconia deposited under a total pressure of 2 kPa and for a ratio $\alpha = 3$. The deposits thus prepared are polycrystalline, with a small grain size (about 0.1 μ m) which increases slightly with temperature. In the same way, they become more homogeneous and dense as the temperature is increased.

Micrographs of zirconia deposits obtained at a temperature of 965 °C, for a ratio $\alpha = 1$ and various total pressures between 2 and 10 kPa are shown in Fig. 6. This parameter seems to have a marked influence on the grain size which increases with deposition pressure from about 0.1 μ m under 2 kPa up to more than 1 μ m under 10 kPa.

4.2. Structural analysis of zirconia deposits

X-ray diffraction patterns give evidence of the occurrence, after cooling at room temperature, of both monoclinic and tetragonal modifications of



(a)

(b)

Fig. 5. Influence of the deposition temperature on the morphology of zirconia deposited under a total pressure of 2 kPa, a total flow rate of 300 cm³ min⁻¹ and a ratio $\alpha = 3$: (a) T = 815 °C; (b) T = 975 °C.



Fig. 6. Influence of the deposition total pressure on the morphology of zirconia deposited under a deposition temperature of 965 °C, a total flow rate of 300 cm³ min⁻¹ and a ratio $\alpha = 1$: (a) P = 2 kPa; (b) P = 10 kPa.



Fig. 7. Room temperature X-ray diffraction patterns of the zirconia deposits for various deposition temperatures (P = 2 kPa, $D = 300 \text{ cm}^3 \text{min}^{-1}$, $\alpha = 3$).



Fig. 8. Room temperature X-ray diffraction patterns of the zirconia deposits for various deposition total pressures (T = 965 °C, D = 300 cm³ min⁻¹, $\alpha = 1$).

zirconia in the thin films deposited on alumina substrates, the ratio of each phase depending on the experimental conditions (see Figs. 7 and 8).

The fraction of the tetragonal phase given by

$$x_{t} = \frac{I_{t}(111)}{I_{t}(111) + I_{m}(111) + I_{m}(11\bar{1})}$$

where $I_t(111)$ is the intensity of the (111) peak of tetragonal ZrO_2 , $I_m(111)$ is the intensity of the (111) peak of monoclinic ZrO_2 and $I_m(11\overline{1})$ is the intensity of the (111) peak of monoclinic ZrO_2 [11, 12] is reported in Fig. 9, for the same total pressure and ratio α , as defined in Section 4.1., as a function of deposition temperature. This plot seems to reveal a marked maximum for a temperature of 975 °C, with a tetragonal phase ratio of 75%. The observation of all the X-ray diffraction patterns, particularly the relative



Fig. 9. Influence of the deposition temperature on the tetragonal ZrO_2 ratio in the deposits at room temperature.

Fig. 10. Influence of the deposition total pressure on the tetragonal ZrO_2 ratio in the deposits at room temperature.

intensities of the various peaks, permits the exclusion of the influence of some preferred orientations in the deposited films, which could result in false interpretation of the diffraction data.

The influence of deposition total pressure on the tetragonal ZrO_2 ratio in the deposit is given in Fig. 10. For both values of total gas flow rates studied here (300 and 420 cm³ min⁻¹), a pressure increase decreases drastically the tetragonal phase percentage down to a negligible value at about 8 kPa. In contrast, the influence of total flow rate is very weak.

The tetragonal modification of zirconia, which is not usually stable under ambient conditions, seems to be stabilized by the CVD process, the extent of stabilization being dependent on the values of the experimental deposition parameters, essentially temperature and total pressure.

4.3. Chemical analysis of zirconia deposits

The observed stabilization of tetragonal zirconia could be explained by the occurrence in the deposit of some contaminants, such as elements originating in the alloy of the reaction chamber wall. This hypothesis has been eliminated, on the basis of a microanalysis performed with an electron microprobe analyser which did not give evidence of any constitutive element of the CVD chamber being present in the deposited films. The only element detected besides zirconium and oxygen was carbon. However, the small amount of carbon actually found in the deposits formed on flat alumina substrates made the study of the influence of the various experimental parameters on the carbon content and eventual stabilization of tetragonalphase ZrO_2 very difficult. Thus, the study of the stabilization of the ZrO_2 tetragonal phase was also difficult.

Raman spectroscopy is a very sensitive method which has been used by Couzi and Cruege to characterize the state of crystallization of carbon (which can be detected down to 0.2%) in C-C composites [13]. C-BN composites have recently been investigated by Hannache *et al.* [14] and SiC-C deposits have been investigated by P. Martineau *et al.* [15] using a Raman microanalyser (laser excitation, 5145 Å) in the same manner. This method is used in the present work to give a further description of the characteristics of ZrO_2 films as a function of deposition parameters.

The Raman spectra of ZrO_2 deposits are reported in Fig. 11 for various deposition temperatures ranging from 815 to 975 °C (the other CVD parameters are defined in the figure). As previously found by X-ray diffraction, the Raman spectrum of a film deposited at 815 °C permits the identification of the monoclinic zirconia which seems to be the only phase. The main lines observed in that spectrum are given in Table 1, and are consistent with those given by various workers for bulk zirconia ceramics [16 - 20]. As the deposition temperature increases, the intensity of the lines of the monoclinic phase decreases and two characteristic lines of carbon occur simultaneously (wavenumbers, 1350 and 1600 cm⁻¹). When the deposition temperature reaches 975 °C, the carbon lines are very strong, the monoclinic ZrO₂ lines



Fig. 11. Raman spectra of zirconia deposits for various deposition temperatures (P = 2 kPa, $D = 300 \text{ cm}^3 \text{ min}^{-1}$, $\alpha = 3$).

TABLE	

Frequency level (from various workers) of the Raman spectrum main peaks for monoclinic ZrO_2

E. Anast B. Papar M. Ashei	tassakis, vicolaou and r [15]	D. R. Ch F. Adar	rke and [16]	M. Ishigame T. Sakurai	s and [7]	Y. G. Ker and W. B. [18]	amidas White	C. M. Phil K. S. Maz	ippi and diyasni [19]	Present w	ork
$\overline{\overline{\nu}}$ (cm ⁻¹)	Intensity	$ar{v}$ (cm ⁻¹)	Intensity	$ar{v}$ (cm ⁻¹)	Intensity	$ar{v}$ (cm ⁻¹)	Intensity	\bar{v} (cm ⁻¹)	Intensity	$\bar{\nu}$ (cm ⁻¹)	Intensity
92	E										
101	E	105	n	102	H	103	u	104	m		
177	s	181	s	179	s	180	s	180	s	180	s
189	c/s	192	s	190	S	192	s	192	s	190	S
222	w	224	w	222	w	224	w	223	w	225	W
315	E	309	w	305	w	308	w	307	w	310	W
335	B	335	Ħ	334	ш	335	ш	337	H	340	m
347	н	349	E	348	m	349	ш	348	ш	350	m
382	B	385	E	381	ä	383	E	382	ш	390	m
476	s	480	s	476	S	476	s	476	s	480	s
502	w	524	w	500	W	503	w	502	w	510	w
537	W	543	w	534	w	539	W	538	w	545	W
559	w	563	w	556	w	561	w	559	w	565	M
616	ш	619	н	615	m	617	ш	617	ш	620	ш
637	ш	636	u	637	E	638	H	638	H	645	E
						755	w				

w, m and s designate weak, medium and strong scattering intensity, respectively.

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TABLE 2

E. Anastassakis, B. Papanicolaou and M. Asher [15]		D. R. Clarke and F. Adar [16]		C. M. Philippi and K. S. Mazdiyasni [19]		Present work	
$\overline{ u}$ (cm ⁻¹)	Intensity	$\overline{\overline{ u}}$ (cm ⁻¹)	Intensity	$\overline{\overline{\nu}}$ (cm ⁻¹)	Intensity	\overline{v} (cm ⁻¹)	Intensity
145	s	148	s	148	s		
178	s			179	s		
188	s			189	s		
222	w			223	w		
262	s	264	s	263	s	265	s
332	m	319	w	332	m		
380	m	404	w	380	m		
473	S	461	w	473	S		
536	w			536	w		
562	w			561	w		
615	w	606	w	615	w		
640	S	643	m	640	s		

Frequency level (from various workers) of the Raman spectrum main peaks for tetragonal ${\rm ZrO}_2$

w, m and s designate weak, medium and strong scattering intensity respectively.

very weak and one line of the tetragonal phase can be observed at 265 cm^{-1} (see Table 2); however, it is very weak.

The influence of the deposition pressure on the Raman spectra under the conditions, T = 965 °C, D = 300 cm³ min⁻¹ and $\alpha = 1$, is shown in Fig. 12. The spectrum of the deposit formed at 3 kPa reveals a mixture of monoclinic and tetragonal (line at 265 cm⁻¹) zirconia phases combined with pyrocarbon. As the CVD pressure increases, the monoclinic ZrO₂ lines become stronger and stronger, the tetragonal line disappears and those of carbon decrease and become rather weak at 10 kPa.

4.4. Discussion

These results confirm the occurrence of weakly graphitized free carbon in zirconia deposits. Its content increases with rising deposition temperature and decreases when the CVD pressure increases. This $C-ZrO_2$ codeposition is not exactly in accordance with the thermodynamic approach which predicts a deposition of pure zirconia [5]. This disagreement emphasizes the importance of the kinetic factors in a CVD process. Here the water formation reaction, which is probably the limiting step of the reaction process, controls the water concentration whose value at the gas/substrate interface is lower than that at equilibrium. As a consequence, the actual situation can be described by thermodynamic diagrams, but with different values of the



Fig. 12. Raman spectra of zirconia deposits for various deposition total pressures ($T = 965 \,^{\circ}$ C, $D = 300 \, \text{cm}^3 \, \text{min}^{-1}$, $\alpha = 1$).

initial composition of the gas phase, probably lower concentrations of CO_2 and H_2 species and higher values of the α ratio [5], giving rise to the reaction

 $CO + H_2 \longrightarrow C + H_2O$

Nevertheless, the influence of CVD temperature and pressure on the carbon yield assessed in the thermodynamic approach is in good agreement with the experimental results previously given concerning the carbon content of the deposit.

Moreover, Raman microanalysis confirms the stabilization of the tetragonal phase zirconia which has been suggested by X-ray diffraction particularly for a deposition temperature of 975 °C and a CVD pressure of 3 kPa. However, the amount of the tetragonal phase in the deposited films seems to be low. The amount of free carbon in the deposits varies with deposition temperature and pressure in the same manner as that observed for tetragonal zirconia, and this could be a determining factor in the stabilization of the tetragonal phase. Nevertheless, the decrease in the tetragonal zirconia ratio for temperatures higher than 975 °C cannot be explained on this basis.

Another important parameter must be taken into account to understand such a stabilization phenomenon: the effect of grain size. In order to study the toughness enhancement in partially stabilized zirconia, Lange *et al.* have recently reported a thermodynamic approach of the tetragonal to monoclinic zirconia transition, in connection with grain size [21, 22]. This approach takes into account not only the chemical free energy variation ΔG_c



Fig. 13. Phase diagram of Lange et al. [20].

associated with that transition, but also the deformation and surface energy variation ΔU_{se} . On this basis, Lange *et al.* define a critical grain diameter D_{c} as a function of these various energy terms including surface energy and interface areas. Only zirconia grains whose diameters are higher than the critical value $D_{\rm c}$ can be transformed from the tetragonal to the monoclinic structure as the temperature is decreased. These workers have been able to plot a phase diagram, reported here in Fig. 13, which gives the ratio of grain diameters D/D_c vs. an energy ratio $\Delta U_{se}/\Delta G_c$ proportional to temperature, for example. According to this diagram, for large size grains, the tetragonal \rightarrow monoclinic transition occurs at relatively high temperature (close to the equilibrium temperature of 1170 °C) with microcracking and twinning; for grains of lower size $(5 < D/D_c < 10)$, the transition occurs at lower temperature with only twinning; and for grains of much lower size $(3 < D/D_c < 5)$, the transition occurs at low temperature without microcracking and twinning. Finally, for very small grains $(D/D_c < 3)$, the tetragonal phase could be stabilized down to room temperature. Such results have also been found by Anderson and Gupta who have shown that the stabilization of the tetragonal modification of zirconia was achieved when the grain size was lower than 0.3 µm [23].

If such an approach, which concerns the bulk material of partially stabilized zirconia, can be extended to the case of CVD thin films, it is possible to explain the observed stabilization phenomenon on the basis of an accurate morphological study of the deposits. The first analysis in this field, previously given in the present paper, permits the following preliminary remarks: (i) the rapid decrease of the tetragonal zirconia content for deposition temperatures higher than 975 °C could be due to the effect of grain size increasing in the CVD films; and (ii) in the same manner, when deposition pressure rises, the resulting increase in mean grain size (from about 0.1 to 1 μ m) could disfavour the stabilization of the tetragonal phase, which is observed experimentally.

5. Conclusion

This experimental approach of the zirconia CVD process has led to a rather accurate study of the main deposition parameters and of their influence on both the process itself (from a kinetic point of view) and some physicochemical properties of the zirconia thin films thus prepared.

On the basis of the high activation energy exhibited by the deposition rate over the whole temperature range studied, a kinetic process controlled by chemical reactions has been assumed, the limiting step being probably the water formation reaction. The kinetic approach has led to the understanding of the occurrence of ZrO_2 -C codeposition under experimental conditions, when the thermodynamic study [5] predicted a pure zirconia deposit. In spite of the unwanted homogeneous nucleation phenomenon, the influence of total pressure and total gas flow rate has been established. A more advanced investigation of the reaction mechanisms would need more results particularly on the reaction order with respect to the main gaseous species.

The microanalysis of the deposited thin films based on various techniques (such as X-ray diffraction and Raman spectroscopy) has shown the possibility of stabilizing the tetragonal modification of zirconia by choosing adequate deposition conditions, *e.g.* a temperature of 975 °C and a total pressure of about 2 kPa. A preliminary explanation of this result, supported by the thermodynamic approach of the tetragonal to monoclinic transition by Lange *et al.*, has been proposed on the basis of the effect of grain size. This interesting correlation must now be corroborated by other investigations (*e.g.* an accurate method should be used to measure precisely the mean grain size in the deposit).

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