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COMPOSITION OSCILLATIONS IN HARD MATERIAL LAYERS DEPOSITED FROM THE VAPOUR PHASE

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Abstract - For the deposition of hard layers on hard metals from the gas phase in the systems Ti-C-B, Ti-N-B, Ti-V-C-O, Ti-Zr-C, Ti-C-N, Ti-C, B-C and Si-C at selected deposition conditions the existence of oscillations was established, which result in a lamellar structure of the layers. As shown by Auger-Spectroscopic analyses the composition of the lamellas changes alternately. Reasons for the lamellar deposition are discussed and a qualitative macroscopic model is presented.

1. Introduction

The existence of oscillating reactions in homogeneous and heterogeneous systems has been known for a long time [1-5]. In spite of constant reaction conditions for the deposition of solids from the gas phase such oscillations can cause periodical changes of composition and structure, respectively, which appear as more or less perfectly formed lamellar structure of the material deposited. Thus FITZER [2] noticed for instance for the deposition of carbides of silicon, boron and titanium together with free carbon layers, which were constructed alternatively from lamellas with changing carbon content. Laminar depositions were also obtained by GULDEN [4] for the coating of spherical particles with SiC in a fluidized bed. Similar effects, which were noticed for the coating of hard metals with hard coatings, have been investigated more in detail in this study. The essential experimental results and the attempt at a qualitative macroscopic explanation are reported now.

2. Experimental

The layer deposition was performed by chemical gas phase deposition (CVD) at normal pressure in the temperature range of 1250 - 1400 K. For this purpose both hot wall and cold wall reactors were used. Moreover layers were also prepared by plasma-activated deposition (PACVD) (rf- and dc-discharge) at total pressures between 0,1 - 1,0 KPa and deposition temperatures below 1173 K. As starting substances the corresponding metal chlorides, hydrogen, nitrogen and benzene or n-heptane, respectively, were used. For the deposition of vanadium containing layers VOCl_3 was used as vanadium carrier as well as ZrI_4 for zirconium containing layers. Commercial WC-Co-hard metal cutting plates were used as substrates. In the case of

deposition of boron containing layers intermediate layers (e. g. TiN, TiC) as diffusion barriers were deposited to avoid interactions between the substrate and the boron containing layer. For the characterization of the layers at first metallographic techniques were used. Commonly, the detection of lamellar structure is possible by optical microscopy after wet chemical etching ($\text{HF}/\text{HNO}_3/\text{H}_2\text{O}$) at straight or inclined sections. With selected examples the layer composition was investigated in detail by Auger-spectroscopy, EDX- and WDX-measurements as well as by X-ray diffraction.

3. Results

In Table 1 the investigated systems are shown, in which layers with oscillating structure could be deposited. Furthermore, in this table also data of layer composition and the used deposition techniques are given.

Table 1 Investigated systems
(CWR-cold wall reactor, HWR-hot wall reactor)

system	deposited phases	method	substrate temperature
Ti-C-B	$\text{TiC}_x + \text{TiB}_2$ (partially poor crystallinity)	CVD, CWR	1300 K
Ti-N-B	$\text{TiN}_x + \text{TiB}_2$	CVD, CWR	1300 K
B-C	$\text{B}_x\text{C} + \text{B}_{25}\text{C}$ ($x = 7$)	CVD, CWR	1300 K
Ti-C-N	$\text{Ti}_x\text{N}_y\text{C}_{1-y}$	CVD, CWR	1300 K
Ti-C	TiC_x	CVD, CWR	1300 K
Ti-V-C-O	$(\text{Ti}, \text{V})\text{C}_{1-x}\text{O}_x$	CVD, HWR	1323 K
Ti-Zr-C	$(\text{Ti}, \text{Zr})\text{C}_x$	CVD, HWR	1323 K
Si-C	Si (amorphous) + SiC (amorphous)	PACVD, CWR rf-discharge	1043 - 1173 K
TiC	TiC_x	PACVD, CWR (dc-, rf-discharge)	< 950 K

From Table 1 follows that a lamellar structure can be formed in the layer both at single phase and at multiphase deposition. In Figs. 1 and 2 the micrographs of two typical examples are shown. The lamella thickness is between 0,1 and 1 μm . In the case of the single phase $(\text{Ti}, \text{V})\text{C}_{1-x}\text{O}_x$ -layers lattice constant measurements, at which a reflex splitting was established (2 lattice constants determinable) were indicative of existent differences in composition in the lamellas.

For the systems Ti-C-B [9], Ti-V-C-O and Si-C it could be established by Auger-spectroscopic measurements at 6°-inclined sections that the composition of the lamellas oscillates.

In Figs. 3 and 4 examples for such oscillations in a $(\text{Ti}, \text{V})\text{C}_{1-x}\text{O}_x$ - and $\text{TiC}_x/\text{TiB}_2$ -layer, respectively, are shown. At the single phase $(\text{Ti}, \text{V})\text{C}_{1-x}\text{O}_x$ -layer the Ti/V-ratio alternates from lamella to

lamella, at the $\text{TiC}_x/\text{TiB}_2$ -layer the C/B-ratio as well as at the Si+SiC-layer the C/Si-ratio alternates. Analogies can be expected for the systems Ti-N-B, Ti-Zr-C, Ti-C-N and B-C. In the case of TiC_x -deposition by PACVD the Ti/C-ratio should oscillate, because these layers were strongly understoichiometric ($x < 1$) according to element analysis. But oscillations could not be detected by Auger-spectrometric analyses [8]. The lamination of the CVD- TiC_x -layer, prepared with a hydrocarbon-mixture (benzene + n-heptane) as carbon supplier, is most probably mainly an effect in structure. It is known, that for the TiC_x -deposition using benzene and n-heptane, respectively, different growth induced textures will be formed (benzene: $\langle 111 \rangle$, n-heptane: $\langle 100 \rangle$) [6, 7].

Fig. 1 $(\text{Ti,V})\text{C}_{1-x}\text{O}_x$ -layer Fig. 2 $\text{TiC}_x+\text{TiB}_2$ -layer Fig. 3 Auger-line scan over a $(\text{Ti,V})\text{C}_{1-x}\text{O}_x$ -layer

Fig. 4 Auger-line scan over a $\text{TiC}_x + \text{TiB}_2$ -layer

The element composition of the heterogeneous depositions determined by Auger-spectrometric investigations shows that the lamellas must be regarded as multiphase systems ($\text{TiC}_x + \text{TiB}_2$ and $\text{Si} + \text{SiC}$, respectively) with phase ratios changing from lamella to lamella.

The finestructure of multiphase lamellas could not be observed by optical microscopy, because of an unsufficient resolution. One can proceed on the assumption that lamellar layers as a rule have a lower grain size than hard material monolayers, which in general show a columnar crystal growth. But in single phase layers with lamellar structure sometimes also epitaxial growth was found (e.g. in the Ti-V-C-O -system), resulting in the formation of columnar crystals, which extend over several lamellas.

Some specific facts, which can substantiate the interpretation of the results, should be mentioned:

1. The first deposited lamella always has that phase composition which is connected with the higher deposition rate in comparison to the composition of the adjacent lamella.
2. The occurrence of lamellar structures is dependent on geometry and flow conditions in the hot wall reactor. High flow rates can lower the lamella thickness and differences in concentration between the lamellas, respectively (e.g. at $\text{TiC}_x + \text{TiB}_2$).
3. High deposition temperatures ($T = 1473 \text{ K}$, Ti-C-B -system) prevent the formation of lamellar structure.
4. With lowering the deposition temperature the thickness of the lamellas decreases.

These facts indicate the phenomenon of oscillating deposition is based on kinetics. The only fact that at a given composition of the gas phase in the initial state and constant deposition temperature, different final states (different compositions of the lamellas) will be obtained, which cannot be explained by a thermodynamically controlled deposition process. The deposition rates in the Ti-C-B -system (Fig. 5), determined experimentally for dependence on flow rate, also point to the existence of kinetically controlled processes. At low B/Ti -ratios in the gas phase no effect of the flow rate on the deposition rate was established.

Fig. 5 Deposition rates
for the system
Ti-C-B, CWR, 1300 K

4. Model of oscillating deposition

For explanation of the lamellar deposition phenomenon a model has been developed by FITZER [2], the main assumptions of which are the existence of a back mixing zone at the solid-gaseous interface and the autocatalytic acceleration of partial reactions in this back mixing zone. Indication of autocatalytic effects in hard material deposition was not found. We are of the opinion that for the material variety of the systems, in which lamellar growth was observed, the autocatalytic concept should probably not be suitable in general. In the following we present a simple model, which explains qualitatively the formation of oscillating concentration fluctuations during deposition without the assumption of autocatalytic effects. The only necessary precondition is the assumption of kinetic inhibitions different in strength at the deposition of those phases or components, which are participants at the oscillations.

Further explanations are made by means of the schematic in Fig. 6, in which the progress of the deposition rate (v) of component A and B is shown as dependent on time.

For the deposition of the component B lower kinetic constraints as well as a deposition rate higher than that for component A are assumed. From the first assumption follows, that the deposition of A and B should reach a steady state after different times t_1 and t_2 (dotted line in fig. 6). At the steady state for the ratio B:A in the solid deposited the following is valid:

$$\frac{n_{B,s}^{st}}{n_{A,s}^{st}} = \frac{n_{B,g}^o - n_{B,g}^{st}}{n_{A,g}^o - n_{A,g}^{st}} = \frac{v_B^{st}}{v_A^{st}}$$

(n - atomic concentration, s - solid, g - gaseous, n^o - atomic concentration at initial state, st - steady state)

Because the deposition rate of B increases more rapidly than that of A, at time t_1 the gas phase composition as well as the solid composition differ from steady state.

Assuming that $n_{B,g}^{t_1} \approx n_{B,g}^{st}$, at time t_1 is:

$$\frac{n_{B,s}}{n_{A,s}} > \frac{v_B^{st}}{v_A^{st}} \quad \text{and} \quad \frac{n_{B,g}^{t_1}}{n_{A,g}^{t_1}} < \frac{n_{B,g}^{st}}{n_{A,g}^{st}}$$

The departure from steady state at the solid-gaseous interface, built up till t_1 , operates as an increase of the initial ratio $n_{A,g}^0/n_{B,g}^0$. Hence till t_2 v_A rises to $v_A > v_A^{st}$ and v_B decreases (full lines in fig. 6), because the total deposition rate must be constant in the steady state. At t_2 it is:

$$\frac{n_{B,s}}{n_{A,s}} < \frac{v_B^{st}}{v_A^{st}} \quad \text{and} \quad \frac{n_{B,g}^{t_2}}{n_{A,g}^{t_2}} > \frac{n_{B,g}^{st}}{n_{A,g}^{st}}$$

Thus till t_2 a gas phase composition has built up, which operates as a decrease of the initial ratio $n_{A,g}^0/n_{B,g}^0$.

Consequently, v_B increases again to $v_B > v_B^{st}$ till t_3 , because by reason of its lower time dependence v_B cannot follow. In the further progress of deposition v_B and v_A oscillate about v_B^{st} and v_A^{st} , respectively, with a phase shifting of $t_n - t_{n-1}$.

Fig. 6 The time dependence of deposition rate (schematically)

5. Discussion of results

The deviation of the deposited materials composition from the composition in steady state (v_B^{st}/v_A^{st}) runs through an extreme value at t_n . Examples of such changes in composition in the deposited layers, established by Auger-spectroscopy were shown in Figs. 3 and 4. According to the oscillation model proposed an asymmetry of the concentration profile in the lamella can be expected, because $t_n - t_{n-1} \neq t_{n+1} - t_n$ ($n > 2$). In the Auger-spectra this effect sometimes appears, but it is not detectable definitely. The formation of a lamellar structure assumes for times of nearly $t_{n+1} - t_n$ the maintenance of an instationary state at the gaseous-solid interface. Estimations of these times from the number of lamellas and the deposition time led to values of up to about 20 s. The unstable state is influenced by the flow conditions at the substrate and should be overcome with increasing gas flow rate. A decay of the concentration oscillations with the deposition time or a decrease of the changes in concentration or their total inhibition could be a consequence. The latter fact was established experimentally in the systems Ti-C-B and Ti-Zr-C. The decay of the oscillations was observed in the Si-C-system.

The discussed concept also enables the explanation of the observed dependence of the lamella thickness on temperature (Ti-V-C-O-, Si-C-system). With decreasing temperature the deposition rates diminish. Provided that the temporal shift until reaching a stationary state of the deposition of B and A is nearly temperature independent, the lamella thickness must decrease.

The detection of oscillations for the deposition of TiC_x under CVD-conditions and simultaneous use of two hydrocarbons (n-heptane and benzene) can be regarded as indirect confirmation of the main assumption of the model presented above, because benzene and n-heptane show a very different deposition behaviour [6, 7].

6. Conclusions

The formation of lamellar structures for the deposition of solids from gas phase is a kinetic effect. A qualitative macroscopic explanation of this phenomenon without specific assumptions is possible under the precondition that at least two partial reactions are differently kinetically inhibited. With the model presented the experimental findings are explainable.

Fundamentally the occurrence of lamellar structures can be expected for deposition, if there are non-equivalent conditions (PACVD) or for the deposition under conditions, which counteract an equilibrium state (low deposition temperature, cold wall reactors).

Besides concentration oscillations also alternating changes in structure can cause a lamellar structure.

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