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Design of Zr(IV) and Hf(IV) Co-Ordination Compounds - Precursors for MOCVD Synthesis of Protective Coatings

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Abstract. Design and creation of new materials with unusual, predictable or predetermined properties become one of the most actual problems of modern applied chemistry. Main demands are discussed, which are made to chemical compounds used in CVD synthesis of functional materials. A division of volatile metal-containing precursors into main classes is given. On the basis of volatility and thermal stability criteria elaborated at IGIC-NASU, we have designed, synthesized and characterized a series of new advanced precursors for Zr(IV) and Hf(IV). Their properties are compared to those of known species. A possibility of formation of requested properties and structure of final materials is shown.

1. INTRODUCTION

In different branches of modern technique and industry a progress and development depend to a great extent on the possibility of application of new materials with predetermined properties. Such materials could be synthesized e.g. by one of the most promising technique - Metal-Organic Chemical Vapour Deposition. Irrespectively, what is applied either a direct thermal destruction of gaseous substances or an interaction of the latter with a solid substrate, or their destruction in high-frequency plasma, laser beam etc., in any case, the volatile and thermally stable to a certain extent chemical compound plays a dominant role. Thus, one of the main problems of modern chemistry is the development of fundamental research on structure and bonding correlation for chemical compounds, and elaboration of industrial chemical processes of high efficiency on this basis.

2. DISCUSSION

It is a well-known fact [1], that chemical substances could be considered as thermally stable and volatile if they possess a property of volatilization and condensation without a composition change at moderate temperatures (below 700-800 K).

It is also necessary to note, that the substances in question must possess a whole combination of properties, necessary for industrial realization of CVD processes in its different variations:

- the already mentioned volatility should be sufficiently high at relatively low temperatures (50—250°C);
- destruction temperatures should be sufficiently low (150—650°C);

- volatile gaseous pyrolysis products, except the final one, should be readily eliminable from the reaction zone;
- they should be non-inflammable in air;
- toxicity of the complexes and their main thermal decomposition products should be as low as possible;
- relatively low costs.

Taking the above into a consideration and analyzing the properties requested above a following classification of CVD precursors could be given [2]:

- compounds with monodentate α -donor ligands (halogenides, alcoxides, amides, α -organometallic compounds);
- hydrides;
- complexes with π -acceptor type ligands (carbonyls, borohydrides, trifluorophosphines);
- organometallic π -complexes (with cyclopentadienyl, arene, allyl ligands);
- inaqueous salts of several acids (carboxilates, nitrates, perchlorates);
- chelate complexes (β -diketonates and their derivatives, dialkyldithiocarbaminates, tropolonates etc.);
- mixed ligands complexes, which usually contain species from the above list.

By elimination of halogenides, hydrides and inaqueous salt of mineral acids the remained part would represent the basis for MOCVD. But only a limited number of elements (usually early transition metals) form substances within each class, providing acceptable volatility and thermal stability parameters both for research and technological demands. Probably, for such elements as Si, B, P, As, Sb, etc., their α -organometallic compounds remains up to now the most acceptable precursors despite several properties limiting their technological applications. To our mind, the most universal ones for d-, f-elements Au and platinum group metals are their chelates and mixed ligand complexes. As well as ligands of different chemical nature (dentate number, nature of coordinating atom, substitutes nature etc.) could be used, it enables us to vary in a wide range the internal characteristics of the complexes (metal-ligand bond energy, central metal effective charge etc.), hence to control their fragmentation pathways, and inter-molecular interaction parameters (crystal lattice type, dipole moment etc.), and in turn to vary their volatility.

We would like to give an example, that illustrates a possibility to design complexes suitable for a purposeful formation of a material with predetermined properties. On the basis of volatility and thermal stability criteria [3,4] we have chosen mixed ligand co-ordination compounds of Zr(IV) and Hf(IV). Bearing in mind the electronic structure of these metals and a derivative of it - high co-ordination number in condensed phases, revealed in a trend to inter-molecular interactions between the central metal atom and donor atoms of ligand's periphery of a neighbour molecule, a formation of closed structures with the maximum steric shielding of the central metal atom are required. Thus, we fixed our attention on metallocene species Cp_2HfL_2 and Cp_2ZrL_2 [4] where L = bicyclic alifatic alcoholato-ligands. Such ligands contain only one donor atom - oxygen bonded to the metal but shielded from other interactions by voluminous and indifferent bicyclo[2.2.1]heptane framework.

In order to resolve some theoretical problems of co-ordination chemistry and to realize a purposeful gas-phase synthesis of materials and films, a knowledge of a series of fundamental precursors characteristics such as their volatility, thermal destruction pathways and products appear to be very important. A combination of some physical and physico-chemical methods was used for this purpose: sublimation temperature determinations, thermo-gravimetric analysis,

mass-spectroscopy (MS) and mass analyzed ion kinetic energy spectroscopy (MIKES). The data obtained are generalized in table 1 in comparison with known species.

Table 1. Generalized data on volatility and thermal stability of new and traditional Zr and Hf precursors.

Type of compound	t subl, °C (1 torr)	tCVD, °C (5-10 torr)	Main final product
MX₄			
β-diketonates	150 - 210	530 - 550	MOC
bicyclic alcoxides	200 - 250	600 - 650	MOC
Y₂MX₂			
alcoxides of metallocenes	140 - 220	600 - 650	MC, MOC, MO ₂

However, these data represent only the initial and final steps of the isolated process, i.e. in absence of any external influences, catalysts, doping agents etc. While a knowledge of its features is of extreme importance from the chemical viewpoint in order to control the thermal destruction process and, hence, a composition of a growing film. Generally the process of thermal decomposition of co-ordination compounds could be considered as that of homopolar bonds dissociation in the complex, which lead to a formation of neutral particles - the metal and radicals or oxygen- and carbon-containing molecules of the metal as a result of in-ligand framework bonds cleavage together with the ligand thermal destruction products. Taking into account a possibility of successive fragmentation these patterns could be represented as follows:

From the other hand, taking into consideration an electronic structure of the complexes viz. delocalization of the electronic density distribution on HOMO the process of their homolytic (eqv. 1) or heterolytic dissociation could be realized with rather comparable probability, although the latter is dominant for the alcoholates. Realization of one or another fragmentation patterns depends in each case on:

- a chemical nature of the central metal atom;
- the nature of the ligands;
- character of chemical bonding metal-ligand;
- presence of periphery substituents in the ligand framework;
- electron-donor or acceptor properties of these substituents;
- the reaction temperature and pressure;
- presence and nature of doping agents,

and several other factors. The most complete image of the complexes in question thermal dissociation could be described on the basis of MS and MIKES data analysis. A particular attention was paid to the metal-containing ions, which are of great interest. Let us consider three characteristic examples of main fragmentation pathways see fig.1 for each class of complex molecules from the table 1.

In order to complete the characterization we have studied a gas phase composition at conditions of thermal destruction of the precursors in an inert atmosphere in a static conditions. The fig. 2 shows a normalized scheme of main decomposition products for one of the designed

Fig.1 Comparison of the most favoured fragmentations for organometallic precursors (see table 1)

precursors, compared to that of tetrakis-acetylacetonate at optimal deposition temperatures of 500°C and 600°C respectively.

Fig.2 Normalized scheme of main decomposition products

Composition of the destruction products could be controlled from one hand by introduction of different substituents into the ligand molecules, from the another - by introduction of doping agents into a gas phase. This first way is rather effective for β -diketonates, but particularly, in our case. Two isomers of the complex $[\eta^5-(C_5H_5)_2M(OCxHy)_2]$ with different positions of substituents in the ligand have the fragmentation patterns contrast up to vice versa - this is the most evident example of the former thesis. The second mode consists of an introduction of doping agents into a gaseous phase (the reactive medium), they could be either generator or traps of free radicals. This lead finally to a stimulation of carbide or oxycarbide phase formation phase formation. Among a wide set of new metallocene dialcoholates with bulky ligand framework synthesized by us the complexes able to lateral ligand elimination as an entity being preferred as precursors to those where the cyclopentadienyl loss is favoured. Thus we have chosen bis- η^5 -cyclopentadienyl Zr or Hf di-

trimethylbicycloheptan[2.2.1]-2-olates with methyl substituents in 1,3,3 and 1,7,7 positions. As a reference we have used traditional representatives - tetrakis-acetylacetonates of Zr and Hf.

The next and not the least among the factors determining a quality of the films obtained are the gas phase temperature and composition. On the basis of an experience of several years of our laboratory (the Ukrainian partner) [3] a temperature regime of the deposition was maintained in the limits 530-560°C and 550-590°C for acetylacetonates of Zr and Hf respectively. It is 650-700°C for mixed ligand metallocenes. As one could expect, at lower temperatures, the incomplete decomposition was taking place, while at the higher ones an increase of a film porosity with the increase of T was observed as well as an adhesion of the film to the substrate is deteriorating. It should be noted, that the lower temperature limit corresponds to compact substrates (e.g. graphite glass) and the higher one - to fibers, composites and porous substrates.

Coatings obtained have a graded character suitable for protective ones [5] which is predetermined by the synthesis conditions - choice of the precursor and gradual variation of the gaseous phase composition. These enables us to solve one of the quite complicated problems - coatings deposition on complex profiles, e.g. inter-fibrous intervals in carbon composite materials. As evidentiate fig.3, they have a complex surface with abundant heights,

Fig.3 SEM micrograph of untreated surface

Fig. 4 SEM micrograph of the sample after the infiltration of pores

Fig. 5 SEM micrograph of the infiltrated sample after thermal shock test.

slips and altitude overfalls of about 200µm. We succeed in deposition of a a graded protective coating in the inter-fibrous and inter-layer intervals accompanied by smoothing of the

surface (fig.4). The samples treated were exposed to thermal shock tests at 1000°C (fig. 5) which shows the resistance of the coating related to its graded structure.

Summarizing the above we would like to emphasize that together with numerous works on traditional precursors and technologies, several specific problems are very difficult to resolve by traditional ways. The molecular design coupled with the actual development of organometallic and co-ordination chemistry are able to find successfully these solutions.

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