

Mechanism of gaseous–phase formation of the film alloys of VI group metals from the carbonyls

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The chemical aspects of the joint thermodissociation of molybdenum and tungsten carbonyls on the NaCl substrates are considered.

It was found that the process of ion-radical centre genesis is a reaction of redox disproportionation type in which the adsorption complexes of donor and acceptor nature are interacting. Such reactions proceed at a quite high rate in condition of bifunctional promoting complex formation. In this case the nature of ion-radical mechanism of the joint dissociation of VI group metal carbonyls enables to explain the basic regularities of the kinetics the morphology and phase compositions as well as the morphology and structure of the formed bimetal films.

The determination of the mechanism of joint thermodissociation of studied metal carbonyls will enable in the future not only to control the composition and structure of the deposited films but also to regulate the former.

The precipitation of the bimetal films from the metal carbonyls in the gas phase is a complex multistage process including a number of diverse stages: vaporization, mass-transport, adsorption, dissociation proper and film formation.

This paper investigates chemical aspects proper of the joint thermodissociation of the Cr, Mo, W and Re carbonyls.

The principal difference of the dissociating systems under consideration, i.e. the co-precipitation of two metals consists in the fact that in all stages and all phases:

gaseous, solid and adsorption layer, - there are

available particles containing the atoms of two different metals. The relations of the components at some stages (vaporization, reactants transport and behaviour in the adsorption layer) will be considered at a quite approximation as additive ones. However the processes occurring in the adsorption layer (chemisorption, activated adsorption, desorption, decarbonylation processes) are to be investigated with regard to the eventual interactions of diverse particles. The basic question is whether such interactions are of substantial importance long since the adsorption layer or they are to be considered only when the metal adatoms being formed in the decarbonylation process are passed into the crystal lattice. So that, the problem of estimation of the reactivity of the considered metal carbonyls in the adsorption layer arises. Therefore their reactivity analysis and estimation are to be carried out.

The displacement of the carbonyl ligands is the mostly important reaction type to consider for the carbonyls as the precipitation process for each every metal atom comes to the displacement of the carbonyl ligands of coordination field by the "new" ligands-atoms of the same or other metal.

It is known that for the metal carbonyls the reaction of nucleophile displacement of the carbonyl ligands by other Lewis bases are very specific. However such reactions are difficult to proceed even in conditions of oxidation degree of the central atom being unvaried.

the table 1 the respective data for the VI group metal and iron carbonyls there are given. as is obvious from the table the dissociation energy of the chromium, molybdenum and tungsten carbonyls exceeds the respective value of the iron pentacarbonyl and that such values are substantially varied with the series Cr<Mo<W.

Besides, in the papers concerning this matter[3] there are the data on the energy of the metal- CO bond in the gaseous metal and CO carbonyls. It is shown that the first CO-ligand decarbonylation substantially from the hexacarbonyls at the electron state. At same time the E_a increase within the Cr<Mo<W series is noted process of full thermodissociation of the $M(CO)_6$ metal carbonyls[4,5]

However for the chemistry of the metal carbonyls are quite characteristic the rebox transformations. Moreover it is shown that in the cation and anion radicals the decarbonylation proceeds at very high rates with subdiffusion constants. There is a entire class of displacement reactions initiated by electron transport [6-8].

Should the redox properties of the $M(CO)_6$ carbonyls be specified firstly there is needed to point on their electrochemical behaviour in the solutions. It is shown [9] that they may be subjected to a reversible single-electron oxidation and reduction with formation of the 17 electrons cation radicals or 19 electrons anion radicals, respectively. From the table 2 it is obvious that during the passage from the chrome positive field. At the same time the variations of the oxidation potentials are quite insignificant[10].

From the above mentioned it is obvious that:

1. In the solutions the both anion and cation radicals of the metal carbonyls exist;
2. The oxidation of the neutral carbonyl molecule proceeds more easily than its reduction.
3. The potentials values of the VI group metals carbonyls reduction are closely spaced and oxidation features are different ones.
4. In the ion radicals the decarbonylation reactions proceed at very high rates.

While the importance of the data concerning the metal carbonyl behaviour in the solutions are very significant but insufficient. To discuss the matters concerning the adsorption layer it is required to have notion about the reactions in a gaseous phase. The $M(CO)_6$ cation and anion radicals are formed in the experiment conditions by electron impact and by dissociation trapping

[11]. As regards to the matters discussed in this paper the information on the multinuclear particles with different metal atoms are very important.

In the paper[12] the observation results of the polymetal carbonyl-cations within the mass-spectrum in the simultaneous admission conditions of the VI group hexacarbonyls is given. The studies were carried out under the 10^5 - 10^6 torr pressure and at 35°C-100°C temperatures. The cations of $CrMo(CO)_n^+$ composition (where $n=5-7$) in the gaseous phase there were found. Also there were found the binuclear complexes for molybdenum and the three-nuclear complexes-for the chrome, and tetra-nuclear carbonylcation clusters -for the tungsten. Also, it is very important that equally with the metalcarbonyl clusters there were found the carbonylcarbide and carbonylcarbide and carbonyloxide clusters of $M_4(CO)_{12}C'$, $M_3(CO)_6C'$, $M_3(CO)_6O'$ types.

So, this investigation carried out, it was shown this the ion radical dissociation chemistry is specific for the chemistry of the VI group metal carbonyls both in the solutions and in the gaseous phase.

In the approach to the analysis of the $M(CO)_6$ carbonyl thermodissociation processes it is necessary firstly to underline that till now the matter of the ratio of divers patterns of such reaction isn't considered in the papers. But some investigations are known where applying high fields technology the growth of the metal dendrites was proceeded by ion radical mechanism[13]. However the experiment conditions in these investigations are substantially different of the bimetal films is carried out in the vacuum chamber of the VUP plant operating at the $1.33 \cdot 10^{-3}$ Pa pressure of the residual gases and provided with set away carbonyl evaporator operating in an independent heating thermostatic mode. The joint steams admission into the reactor at 60-110°C temperatures was carried out. the substrate temperature varied from 450°C to 650°C. There was used the EPR thermodissociation investigation method was used basing on the model system which was an ampule of carbonyl evacuated at 10^3 torr pressure and heated up to 700°C in the pulse operation mode.

The experiment conditions mentioned in the paper[14] are more close to the our one and

where the iron filiform crystals were obtained from the respective carbonyls. The author proposes the model of a chained ion-radical mechanism of the iron carbonyl thermodissociation which consists of three basic stages: chain springing-up in which the main role is played by electron transport resulting in the source of active iron-carbonyl radicals; chain extension and formation of the α -Fe structure as well as the chain breakage, filiform crystals high-speed growth stopping resulted of the ion-radical centers destruction. We attempted to apply this model in our conditions. the main problem here consists firstly in the fact that the "electrochemical slits", i.e. $E = E_{1/2}^0 - E_{1/2}^0$ for the $M(CO)_6$ is substantially higher than for the iron carbonyl and the reduction potentials are more negative. In particular, for the $Fe(CO)_5$ the $E_{1/2}^R = -1.63V$, i.e. it is shifted by 400–600mV to the positive field in comparison with the $E_{1/2}^0$ for the $M(CO)_6$ [15].

On the other hand, as we carried out the precipitation of divers carbonyls of different redox characteristics, then it may explain the electron transport reaction proceeding.

The substantial factor is the fact that we used the ion substrates which surely, will promote the redox processes. Indeed it is known[16] that the application of the iron carbonyls on the sel substrated (NaCl, Kbr, CsI) results in its redox disproportionation. All these factors served as a support base to elaborate the mechanism model proposed below. For simplification purposes the pattern of the bimetal film formation process was investigated basing on the $Mo(CO)_6$ - $W(CO)_6$ system and as a substrate was proposed below chips of rock salt of oriented growth<III>.

The first stage of the process is the adsorption on the substrate surface of the metal hexacarbonyl molecule evaporated from the gaseous phase or entered from the adsorption layer (Physically adsorbed molecule). Unlikely to the paper[15] it isn't needed to postulate the existence of additive active donor center with which the molybdenum hexacarbonyl molecule interacts as the role of the centers in our case is played by the chlorine ions: the coordination being implemented by participation of one of the carbonyl ligands and the bond of oxycarbene type is occurred. The chemisorption of such type was observed by

V.G.Kuleshov, G.A. Domrachev and B.V. Zhuk[16] when investigating of the $Cr(CO)_6$, $CpMn(CO)_3$ carbonyl complexes adsorption by reflectance-adsorption IR spectroscoph.

It may be believed that the electron couple of active surface center is entered on the loosening orbitals $4e''$ and $9a''^2$ having substantially $CO\pi$ nature. It results in that the adsorption complexes acquires a reduction features. The phenomenon of reduction capacity increase in result of the ion nucleophile addition to the carbonyl ligand adatom $Mo(CO)_6$ is well known.[18]

The second state of the proposed pattern is an electron transport from this complexes to the physically adsorbed molecule of tungsten hexacarbonyl. There was assumed such direction proper of the electron transport because the $W(CO)_6$ reduction potentials are lower ones.

This process is followed by a splitting out of two CO molecules from the occurred ion-radicals: So that, on the surface there are occurred the reactive particles with open electron shell. In general the process of ion-radical genesis is a reaction of redox disproportionation type in which the adsorption complexes of donor and acceptor natures participate. In this case the donor or acceptor matures are determined by the adsorption center type (Na^+ , Cl^-) which participate in the electron redistribution (disproportionation) process. In certain sense it may be say on the electron passage in the couple Na^+ , Cl^- , catalyzed by two $Mo(CO)_6$ molecules and arised surface $NaCl$ 'pseudomolecule'. Such reactions proceed at a quite rate and need only for bifunctional activating complex formation. In our case the substrate nature proper simolifies such disproportionation. and then the chain extension at expenses of the ion-radical interactions with the $Mo(CO)_6$ neutral molecules is occurred. In such process in the adsorption layer there are arised the mixed clusters of different mature and nuclear features, e.g:

The composition, charge, metal fractions in the ion-radical clusters within the adsorption layer may vary within a quitely wide range. It is to take into consideration that the open electron shell results in their easy exchanges by their ion-carbonyl fragments. So that, in the adsorption layer there is occurred a quasi-equilibrium state of the entire blocks-clusters. In these cases the lattice proper will determine the direction of the take-off from its feeding layer.

The above mentioned initiation mechanism is applicable for the ion-radical genesis on the ion substrate only. However as the film thickness increases its effect is progressively decrease. In such cases the initiation isn't occurred at the substrate lattice nodes but at the additive centers occurred in result of the metal carbonyls of different nature, However in such cases the initiation reaction proceeds with more difficult, at lower rates and in more degree it is depending on the temperature. A selective nucleating centers growth.

The occurrence in the adsorption layer of divers ion-radical clusters promote formation of the carbonyl-carbide and carbonyl-oxide particles. By analogy with the gaseous phase the tetranucleous cation-radical clusters play role of oxygenation particles:

In accordance with this proposed model the reaction has an ion-radical chain process in its nature with a redox initiation occurring on the base of the activating complex formation pattern and proceeds at a quite high rate. To this model the rocky kinetic curves are corresponding for the dissolution degree (α) of the molybdenum and tungsten carbonyls (fig.1). The induction period changes into the exponential phase of dissociation. Such type of kinetic curves agrees with the model of chain mechanism. The film structure formation is occurred by blocks when the bimetal ion radical clusters formed in the adsorption layer are built in the lattice losing a part of carbonyl ligands but conserving its ion-radical reaction center.

Referred on the above mentioned one automatically makes conclusion that the chemical composition of the film is determined firstly by its thermodynamics. In this case the kinetics isn't limiting the analysis of the coating film composition enabled to observe its independence on the initial ratios of the entered metal carbonyls in the reaction. The composition is determined only by the substrate temperature which so is limiting the mature of the clusters take-off. In such cases there is occurred the building-in of the clusters of specific composition only and their orientations in the crystal lattice are very random. One phase (cluster) is building in the crystal lattice of the other one but the structure building up isn't yet accomplished. Within the film in formation the dislocations and doubles' formation zones are developed (fig.2).

The observed faults are resulted of the block formation mechanism.

In the film structure formation owing to the redox properties of the molybdenum and tungsten carbonyls there is possible the formation of the blocks notable in some cases for high content of tungsten and in other cases-for high molybdenum content but during the structure stabilization the exchange process between them is occurred because referred on the state diagram such systems within all concentration ranges are the solid displacement solutions.

Conforming to the proposed mechanism in the structure formed at lower temperatures (400°C) there will no occur and indeed aren't observed any occurrences of the addition phases. However at higher temperatures (600°C) owing to the atom diffusion in the lattice the formation of the carbide and oxide addition structures is occurred that is confirmed by the results of electron microscopy.

Within this proposed mechanism there is explainable the existence of two structure types, namely stratified and column ones (fig.3). Such differences are determined by different mechanisms of the initiation reaction. It will be incorrectly to use the motions only of local donor centers. with the substrate temperature increase the occupation of highly located vacant electron levels within conductance zone is occurring that creates favourable conditions to transport the electron into the adsorbate molecule:

The real donor of the electrons is an atom group which is located in the surface layer of the crystal lattice. This atom group proper forms with adsorbed molecule a "surface" cluster. It determines the formation of the films having structures of column type.

So, the proposed model of the ion-radical mechanism of the joint dissociation of the VI group metal carbonyls enables to explain the basic regularities of the dissociation kinetics, chemical composition and their morphology.

Energy of mononucleous metal carbonyl dissociation [2]

Compound	Energy of dissociation, kJ/mol
Cr(CO) ₆	124
Mo(CO) ₆	152
W(CO) ₆	178
Fe(CO) ₅	117

Electrochemical specifications of the VI group metal carbonyls

Metals	$E^R_{1/2}$	$E^U_{1/2}$
Cr	-2.29	1.53
Mo	-2.11	1.53
W	-2.04	1.53

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Designations concerning the figures:

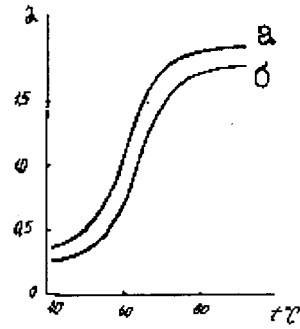


Fig.1 Kinetic curves of molybdenum (a) and tungsten (b) carbonyl dissociation

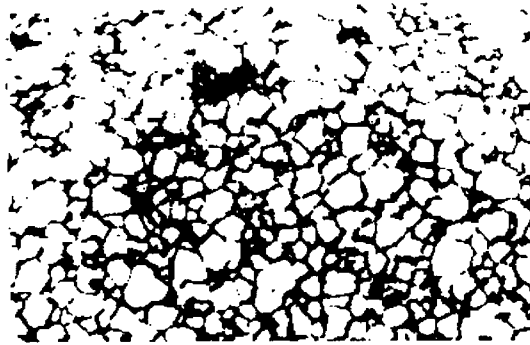
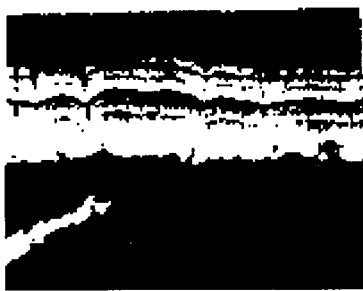


Fig.2 Structure of bimetal carbonyl film, 1000x



(a)



(b)

Fig.3 Interior structure of the bimetal film formed at 400°C (a) and 600°C (b) the substrate temperatures.