

Possibilities of Preparation of Coatings from Carbonyls

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-----ABSTRACT-----

The authors characterize the carbonyl functional groups and the methods of their preparation used in the deposition of coatings applied to the functional surfaces of mechanical components. The processes of decomposition of carbonyls are presented. The authors present decomposition curves of carbonyls. Briefly and concisely describe CVD and PECVD methods of coatings deposition. Article presents the results of research focused on coatings from carbonyls.

KEYWORDS: Carbonyls, coatings, PVD, CVD, PECVD

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I. INTRODUCTION

Carbonyls are often used as precursors used in coatings deposition due to their high hardness, low coefficient of friction, high corrosion, oxidation and abrasion resistance and many other properties. They are deposited on the functional surfaces of machine parts, on the surface of mechanical parts made of steel, on cutting and forming tools. Coatings can be applied by these methods: **PVD** (Physical Vapor Deposition) methods and **CVD** (Chemical Vapor Deposition) methods

It is also possible to use a combination of the above methods of deposited of coatings, which can be combined into 1 deposition process. We refer to this combination of methods as hybrid technologies of deposited coatings, which are increasingly being used in practice. Among the most used deposition methods of carbonyls are PVD methods, namely Direct Current Magnetron Sputtering (DCMS) [1-3], Radio Frequency Magnetron Sputtering (RFMS) using various gases, most often with argon [4-5]. The carbonyls can be also deposited by the High Target Utilization sputtering method (HiTUS) [6] and by the High Power Impulse Magnetron Sputtering method (HiPIMS) [7].

Carbonyls can be deposited by CVD methods too. The big disadvantage of CVD methods is the high deposition temperature (800 °C – 1200 °C), which does not allow the deposition of coatings on aluminum and its alloys, due to its low melting point (660 °C). This group of methods includes the PECVD (Plasma Enhancing Chemical Vapor Deposition), which provides us with lower deposition temperature and is suitable for deposition of other carbonyls [8].

II. CARBONYL FUNCTIONAL GROUP AND DECOMPOSITION PROCESS OF CARBONYLS

The carbonyl functional group, simply carbonyl (fig.1a), consists of carbon doubly attached to oxygen and has the chemical structure C = O. By attaching various substitutions to carbon, it is possible to obtain many different types of functional groups, such as ketones, aldehydes, esters and carboxylic acids [9].

Ketones (fig. 1b) are molecules, where 2 hydrocarbon residues are attached to the carbon [9].

Aldehydes (fig. 1c) are molecules, where hydrogen and a hydrocarbon residue are attached to a carbon.

All of these species contain a C = O bond but differ in the nature of the substituents. There are some influences that affect the chemical structure of C = O bond, such as hydrogen bonds [9]. Figure 1 schematically shows the structure of carbonyl groups [9]:

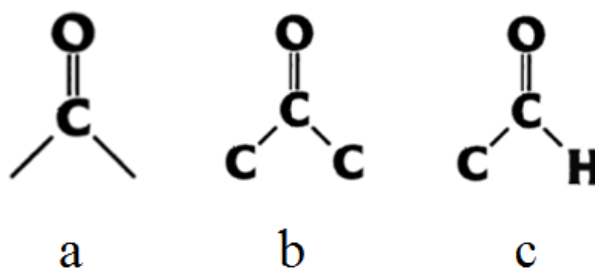


Fig. 1 Structure of carbonyl groups [9]

The shape and the position of a decomposition curve of Mo (CO)₆ depend on the investigated complex and on the applied experimental conditions. By increasing the gas flow rate, the average time the complex spends in the tubular flow reactor decreases and therefore a higher temperature is needed for a complete decomposition process (fig.2) [10]. The rate of decomposition affects the CO content of the carrier gas, indicating that the low CO content suppresses reversible decomposition in the gas phase. High concentrations of CO promote the reversibility of homogeneous dissociation of the Mo – CO bond due to a higher probability of feedback, with the decomposition curves shifting towards higher temperatures [10]. Finally, regardless of the gas flow used and its composition, the decomposition reaction Mo (CO)₆ begins at a temperature of 250 °C, given by the following equation [10]:

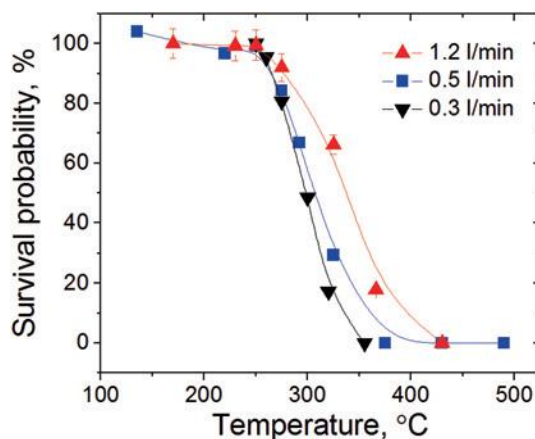
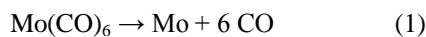


Fig. 2 Decomposition curves of Mo (CO)₆ obtained at different gas flows [10]

Compared to what was previously determined for Mo(CO)₆, higher carrier gas flows shift the decomposition curves of W(CO)₆ (fig.3) to higher temperatures. The reduction of the CO content from 50% to 16% did not show a significant effect on the decomposition behavior of W(CO)₆, which supports the assumption of preferred heterogeneous decomposition at selected high CO concentrations [10].

The decomposition reaction of W(CO)₆ starts at approximately 350 °C, which is a 100 °C higher temperature compared with decomposition reaction of Mo(CO)₆. W(CO)₆ is formed by the equation 2 and the decomposition reaction is given by the equation 3. On the figure 4 is a comparison of decomposition curves of Mo(CO)₆ and W(CO)₆ [10]:

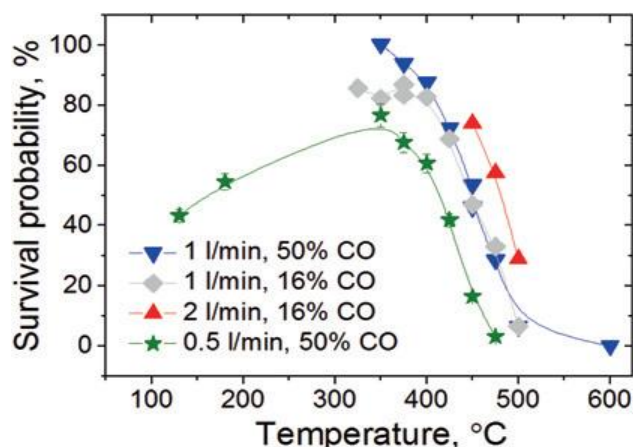
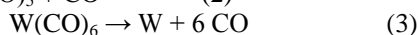
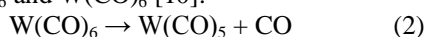


Fig. 3 Decomposition curves of W(CO)₆ obtained at different experimental conditions [10]

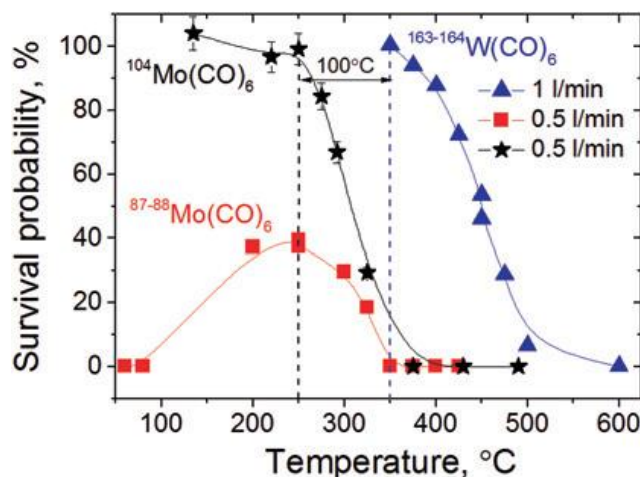


Fig. 4 Comparison of decomposition curves of Mo and W carbonyls [10]

III. CVD AND PECVD DEPOSITION METHODS OF COATINGS FROM CARBONYLS

Chemical vapor deposition (CVD) is deposition process in which precursors in gas phase undergo dissociation and chemical reactions to form a stable coating in an activated plasma environment at temperature in range of 800 °C to 1200 °C. The kinetics of the CVD process involves many steps, that determine the rate of the deposition process. They are [11-13]:

1. the homogeneous reaction taking place between gas molecules in a reaction chamber
2. the heterogeneous reactions occurring on the surface of the substrate
3. mass transports of gaseous precursors and formation of coating

The **advantages** of CVD methods include the high deposition rate, high density and purity of coatings, excellent adhesion of coating on the substrate, good wear resistance, good corrosion resistance and others [11-13]. The **disadvantages** of CVD methods include the high temperature of deposition, instability of substrates at high temperatures, formation of by-products, that are toxic and dangerous to humans and others [11-13].

The **PECVD** process involves the production of plasma by electricity, as opposed to the use of a heat source in the CVD process. Plasma is a mixture of electrons and neutral particles. Both working and reactive gases enter the PECVD process. One way of plasma formation is gas heating, where ionization temperatures are extremely high, which is limiting for PECVD process. A more efficient way to generate plasma is to use electricity at different frequency discharges, which can be divided into [11-13]:

- a) **audio frequency**, where the frequency discharges are in the range of 10 - 20 kHz
- b) **radio frequency** (referred to as RF), where the frequency discharges for plasma generation are 13.56 MHz
- c) **microwave frequency**, where the frequency discharges are value of 2.45 GHz

The **advantages** of PECVD include the lower temperature compared to CVD methods (400 °C and less), possibility of depositing of organic and inorganic materials as precursors, thermal and chemical stability of coatings, high resistance of coatings to solvents, high resistance to corrosion and oxidation and others [13]. The **disadvantages** of PECVD include instability of coatings against moisture and aging, existence of compressive and residual stresses in coatings and others [13]. The figure 5 shows the carbonyl interaction with surface of substrate and the figure 6 shows the RF PECVD process [14].

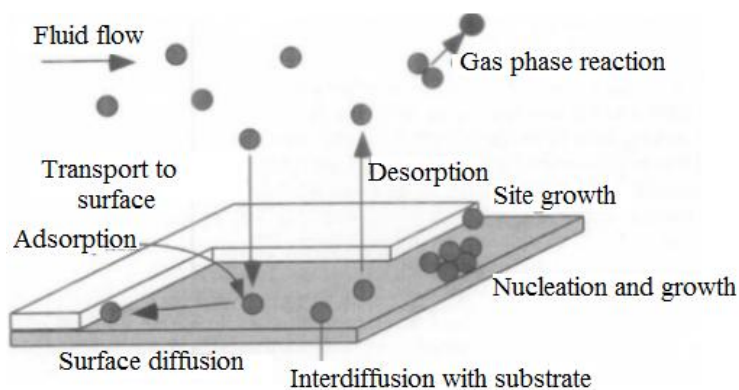


Fig. 5 The process of carbonyl interaction with surface of substrate [14]

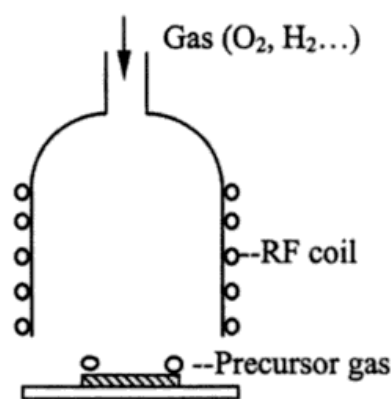


Fig. 6 The RF PECVD process [14]

IV. PUBLISHED EXAMPLES OF COATINGS FROM CARBONYLS

As already mentioned in the introduction, coatings from carbonyls can also be applied by PVD, CVD and PECVD methods. Table 1 presented WC/C coatings deposited by Direct Current Magnetron Sputtering (DCMS) method by various authors at different deposition conditions [15-20].

Rebolz et al. [15] studied a WC/C coating, deposited by the DCMS methods. They got the maximum values of $H = 40$ GPa and $E = 300$ GPa with 15% carbon content. Wänstrand et al. [16] presented a WC/C coating deposited by the direct current magnetron sputtering (DCMS) methods. They used temperature in range $200\text{ }^{\circ}\text{C}$ - $250\text{ }^{\circ}\text{C}$ during the deposition and the pressure of vacuum chamber in range $0,4 - 0,8$ Pa and the value of bias 200 V. They evaluated the mechanical and tribological properties of WC/C coating. The values are presented in table 2. Palmquist et al. [17] evaluated the concentration dependence of C of WC/C coating, which have been deposited on 3 substrates. H, E and COF (Table 2) were evaluated. Maximal values were $H = 25$ GPa and $E = 450$ GPa at 35 at. % C. Su et al. [18] used the monocrystalline Si substrate to test structural properties under laboratory conditions. Zhou et al. [19] evaluated of WC/C coating at $C = 75\%$. They measured the values of mechanical (hardness H, Young's modulus E) and tribological (COF) properties, which are presented in table 2. Czyniewski et al. [20] evaluated WC/C coatings in relation to the content of carbon in the layer. Acetylene flow was varied and the maximal value of $H = 42$ GPa was measured at the concentration of $C = 33,7\%$.

Table 1: Deposition conditions of WC/C coatings [15-20]

Deposition conditions of WC/C coatings					
Authors	Deposition methods	Substrate	Temperature [°C]	Pressure [Pa]	Bias [V]
Rebolz C.	DCMS	AISI 316	350	0,14 - 0,16	50
Wänstrandt O.	DCMS	HSS	200 - 250	0,4 - 0,8	200
Palmquist J.P.	DCMS	Al ₂ O ₃	450	0,20	300 - 350
Su Y.D.	DCMS	Si	-	-	0-200
Zhou S.G.	DCMS	Stainless steel	-	10 ⁻³	300
Czyniewski A.	DCMS	100Cr6 steel	150	0,3-0,4	100

Table 2: Mechanical and tribological properties of WC/C coatings and their values [15-20]

Measured properties of mechanical and tribological properties of WC/C coatings				
Authors	Thickness [μm]	E _{IT} [GPa]	H _{IT} [GPa]	COF
Rebolz C.	3	210 - 300	15 - 40	0,7
Wänstrandt O.	2,0 - 4,0	-	15 - 18	0,35
Palmquist J.P.	0,5	300 - 450	14 - 25	-

Su Y.D.	-	-	32 - 47	-
Zhou S.G.	2,1	281	24	0,12
Czyzniewski A.	3,0 - 3,5	140 - 460	14 - 42	-

V. CONCLUSIONS

The properties of coatings from carbonyls are influenced by various factors. These are the deposition parameters, namely the chamber pressure, the substrate temperature, the bias value, current flow, ratio of working (Ar), reactive (N₂, SiH₄) gases and many other parameters. Argon is built into the coating as in a grid (cavities and between nodes) and causes an increase in internal compressive stresses and thus hardness. Reactive gas N₂ is present in the coating as nitride, which is hard and thus contributes to the increase in hardness. During PVD evaporation and sputtering process, the position of the coated surface relative to the target affects the mechanical and tribological properties. With the vertical impact of the particles on the coated surface, the properties of the coating are optimal (thickness, hardness, COF, structure, ...). In particular, the thickness decreases with increasing angle of deflection from 90 °.

In CVD, the position of the coated surface in the vacuum chamber does not affect the thickness and thus the other mechanical, tribological properties and the texture of the coating, because the precursors are in the gas phase. The coatings prepared from carbonyls have an excellent combination of mechanical and tribological properties, such as high hardness, a high young's modulus, a low COF, high corrosion, and oxidation resistance and more. They can be used in:

A) engineering production:

- as hard abrasion-resistant coatings based on nitrides, carbides, and borides (W, Cr, Mo..) and others, for example to extend the life of cutting tools
- as thermal barriers used to extend the life of aircraft engines (stator blades of jet aircraft), etc.
- to adjust the coefficient of friction of the friction pairs – GLC (graphite like carbon) or DLC (diamond like carbon) coatings

B) electrical engineering:

- in the production of microelectromechanical parts (MEMS)
- in the production of nanoelectromechanical parts

C) optical engineering:

- coatings deposited on the surface of optical instrument lenses and sunglasses to filter out the required spectrum of electrical magnetic radiation

The coatings are often the only and affordable way to achieve the desired properties of functional surfaces.

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