## Thermal dissociation of iron carbonyls during growth of iron whiskers

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Methods for the preparation of iron whiskers in chemical transport reactions of thermal dissociation of iron penta- and dodecacarbonyls and carbidocarbonyl clusters  $Fe_5C(CO)_{15}$  were described. The morphology, structure, and chemical composition of the whiskers were studied. The main factors determining the growth rate and mechanical properties of the whiskers were revealed. A model for the mechanism of thermal dissociation of iron carbonyls was proposed. This process was shown to be a chain radical ion reaction initiated *via* the scheme of activating complex formation. Analogies between the thermal dissociation of iron carbonyls in the adsorption layer and the known radical ion processes in the liquid and gas phases were found.

Key words: whiskers, iron carbonyls, thermal dissociation, reaction mechanism.

Metal whiskers are characterized by high ratios (20-25) of the length to apparent diameter and represent a peculiar type of inorganic material finding wide use in the recent time due to its perfect crystal structure and, as a consequence, a high mechanical strength, a considerable resistance toward oxidation, and unique electrophysical properties. In particular, they are used for the development of new composite materials with metallic and polymeric matrices and for the production of magneto-dielectric cores and high-efficiency emitters.<sup>1</sup>

Different methods for growing metal whiskers in the solid, liquid, and gas phases are known. Of these methods the simplest and most promising is the gas-phase thermal dissociation of metal carbonyls during a transport reaction in which the chemical nature of the starting components changes. The formation of small amounts of iron whiskers (IW) from iron pentacarbonyl (IPC) and hydrogen was observed for the first time in a chamber of an electron microscope.<sup>2,3</sup> However, lacking data on the mechanism of metal carbonyl dissociation did not allow a preparative method of  $\alpha$ -iron IW preparation to develop. The purpose of this work was to search for optimum conditions of preparing  $\alpha$ -iron whiskers from iron carbonyls, to reveal the main factors affecting the formation of the structure, chemical and phase compositions of iron whiskers, and to establish a scheme of thermal dissociation of metal carbonyls.

## Experimental

Iron pentacarbonyl  $Fe(CO)_5$ , iron dodecacarbonyl  $Fe_3(CO)_{12}$ , and carbidocarbonyl cluster  $Fe_5C(CO)_{15}$  were used as starting compounds for studying thermal dissociation.

Industrial IPC was purified by distillation.

**Iron dodecacarbonyl** was synthesized by refluxing IPC and triethylamine in an aqueous solution followed by treatment with hydrochloric acid and purified by washing with water, methanol, and hexane.<sup>4,5</sup>

Iron carbidocarbonyl cluster  $Fe_5C(CO)_{15}$  was synthesized according to a previously described procedure.<sup>6,7</sup>

All carbonyls used are volatile and easily decompose, which makes it possible to significantly decrease the temperature of thermal dissociation compared to that, *e.g.*, of oxides, to reject the use of explosive and corrosion-active media (hydrogen, chlorine, *etc.*), and to use supports of different shapes. Wire and plates of different steels, Nichrome, and molybdenum, carbon rods, and ceramic tubes served as support materials.

The temperatures of a support and a forming iron sublayer were measured on a VIMP-015 optical micropyrometer with an accuracy of  $\pm 50$  °C.

The residual pressure in a decomposition system was measured with a VT-2A-P vacuum gauge.

Electron microscopic analysis was carried out by transmission and scanning electron microscopy on SEM-505 (Philips) and HU-I25 (Hitachi) microscopes. The accelerating voltage was 20-35 kV.

The chemical composition of the metallic sublayer was monitored on an EDAX X-ray energy-dispersion spectrometer mounted on an SEM-505 microscope.

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ESR spectroscopic study was carried out on an ERS-221 instrument in the X range (~9.45 GHz) with a high-frequency field modulation of 100 kHz.

Apparatus for IW synthesis. Thermal dissociation of iron carbonyls affording iron whiskers was performed in reactors of two types developed by us. The first reactor is horizontal with a tangential supply of a metal carbonyl vapor; it was designed for studying liquid iron pentacarbonyl. The second reactor is designed for studying solid metal carbonyls; it differs from the first-type reactor by the presence of a sublimator (instead of an evaporator) to vaporize iron carbonyls and by the mode of supplying the vapors to the support (along the normal).

Since the thermal dissociation of iron carbonyls to form IW is a chemical transport reaction in which a vapor of the substance under study is transported from a "cool" zone to a heated support, both types of reactors were included into a technological scheme containing a system of valves and connections to control a vapor flow of metal carbonyls, units of condensation and additional decomposition of unreacted substances, devices for combustion of evolving CO, instruments for the temperature and pressure control during the process, a pump, and some other units. The support was electrically heated.

Procedure for preparation of iron whiskers from Fe(CO)<sub>5</sub>, Fe<sub>3</sub>(CO)<sub>12</sub>, and Fe<sub>5</sub>C(CO)<sub>15</sub>. The starting sample as a wire or a plate was purified from contaminations, weighed with an analytical balance, and mounted between electrodes of a vacuum chamber, which was hermetically closed and evacuated with a vacuum pump to a residual pressure of  $9 \cdot 10^{-3}$  Torr. Then the sample was heated at a specified temperature for 1-1.5 h. When an experiment was carried out with crystalline iron carbonyls, the sublimator was simultaneously heated to increase the vapor pressure of the substance under study. Iron carbonyl vapor was transported to a heated support by a system of valves and decomposed on the support to form IW. The residual IPC vapor and evolving carbon monoxide were utilized in additional decomposition and after-burning systems. An observation window of the reactor made it possible to monitor the course of experiment. After the end of experiment, the whole system was cooled to room temperature, the chamber was opened, and the resulting sample was weighed and examined.

ESR procedure for studying the thermal dissociation of iron carbonyls. An ampule 2–2.5 mm in diameter was pre-evacuated to  $10^{-3}$ -10<sup>-4</sup> Torr, filled with a small amount of Fe(CO)<sub>5</sub> or small crystals of  $Fe_3(CO)_{12}$  or  $Fe_5C(CO)_{15}$ . Then the ampule was again evacuated and sealed (without thawing out the mixture). The thermal dissociation of iron carbonyls was carried out for 1-10 s at ~1000 °C until iron traces or an iron mirror appeared on the ampule walls. A longer heating resulted in the appearance of a considerable amount of a ferromagnetic phase, which strongly impeded ESR spectra recording. Iron carbonyl vapor in only one end of the ampule were subjected to decomposition. After heating, the ampule was rapidly frozen to the liquid nitrogen temperature (-196 °C) and placed in a resonator of an ESR spectrometer. The temperature of a standard sample of  $Cr^{3+}/MgO$  with g = 1.97965 was always maintained at 20 °C. ESR spectra were recorded at temperatures from -196 °C and higher. Signals were assigned on the basis of comparing the data obtained in this work and published results for the behavior of iron carbonyl radical anions in solution and adsorption layers.

## **Results and Discussion**

The thermal dissociation of IPC,  $Fe_3(CO)_{12}$ , and  $Fe_5C(CO)_{15}$  in the gas phase affords iron whiskers. Each of the three starting substances is characterized by specific regularities of IW growth. A single crystal character of the obtained IW was established from the electron microscopic and electron diffraction data. The diffraction pattern obtained in an electron microscope (accelerating voltage 100 kV) for a single whisker and its interpretation are presented in Fig. 1.



Fig. 1. Diffraction pattern of a particular  $\alpha$ -Fe single crystal containing a twin in the plane (121) and interpretation of the pattern (black points indicate reflections from the matrix, light points show reflections from the twin, and sign "+" indicates reflections caused by double reflection).



Fig. 2. Interpretation of the cutting and the scheme of planes of an  $\alpha$ -Fe single crystal.

The single crystals can contain twins and other surface defects, for instance, growth steps decreasing the strength of the IW. The average tensile strength of  $\alpha$ -Fe whiskers is 3309 MPa.<sup>1</sup>

The main crystallographic directions of the growth of  $\alpha$ -iron single crystal are <100>, <111>, or <110>. Such an ambiguity is due to a rotation of the diffraction pattern with respect to the image of single crystals at an unknown angle.

The microphotograph of a particular  $\alpha$ -Fe single crystal and the scheme of planes in a cubic lattice are presented in Fig. 2. In all cases, when the direction of IW growth perpendicular to the most densely packed (in bcc lattice) plane (111) is retained, the completion of the planes of the family {110} occurs, transforming the crystal into a pyramidal cube. This can be explained by a considerable local and volume nonequilibrium character of crystallization.

The analysis of the microphotographs of the support surface on which IW grow (Fig. 3, a, b) indicates that the shape of IW "nuclei" composing the sublayer surface corresponds to the shape of the single crystals themselves.

All IW grown by us can be divided into two main types: rectangular with an average length of  $60-70 \ \mu m$  and  $d = 0.5-1.0 \ \mu m$  (Fig. 4) and cone-like IW achieving a length of 120  $\mu m$  and having the so-called "growth drop-let" at the vertex (Fig. 5).

The morphology and, hence, the mechanical and electrophysical properties of IW depend substantially on the conditions of synthesis.<sup>8–20</sup> Of the whole variety of technological factors that can affect the growth and formation of IW obtained by different methods (both physical and chemical), the following factors are usually distinguished as main: temperatures of the support and carrier gas, a saturated vapor pressure of the starting substance in the system, the presence and rate of the carrier gas, the concentration of the starting substance vapor, initiating additives (to supports or gas), the composition of the support, and others.<sup>8–10,21–23</sup>



**Fig. 3.** Microphotographs of the support surface: (*a*) high growth rate of IW and (*b*)  $\alpha$ -Fe whiskers growing on the support surface.



**Fig. 4.** Rectangular  $\alpha$ -Fe whiskers with different directions of growth obtained at a temperature of the support of 1000 °C and an IPC pressure of  $1.5 \cdot 10^{-1}$  Torr.

Let us consider the temperature effect on the thermal dissociation of iron carbonyl vapor under its constant partial pressure.



**Fig. 5.** Conic  $\alpha$ -Fe whisker with a "droplet" at the vertex obtained at a temperature of the support of 1050 °C and an IPC pressure of  $5 \cdot 10^{-1}$  Torr.

The decomposition of iron carbonyls on the support and the formation of a metallic layer start at relatively low temperatures. For example, IPC decomposes already at 200 °C. Iron dodecacarbonyl Fe<sub>3</sub>(CO)<sub>12</sub> sublimes at 60 °C and begins to decompose at 110 °C, while for Fe<sub>5</sub>C(CO)<sub>15</sub> these temperatures are 80 and 250 °C, respectively.

We studied the decomposition of iron carbonyls in a wide temperature range from 200 to 1150 °C. The results obtained for the decomposition of liquid IPC in a low-temperature interval (200–600 °C) agree completely with the published data.<sup>24,25</sup> When the temperature increases from 200 to 600 °C, the globular character of the coating is retained, a crystalline surface is formed, crystals grow, and large spheroids transform into finer semispheroids, which further transform into numerous crystals uniformly distributed over the iron coating surface.

The decomposition of solid  $Fe_3(CO)_{12}$  and  $Fe_5C(CO)_{15}$  under these conditions was studied for the first time. As in the case of IPC, IW are not formed in a low-temperature interval, and only the formation of a metallic coating is observed. In the case of  $Fe_3(CO)_{12}$ , the character of this coating changes with temperature in this interval as follows: at first agglomerates of crystallites  $12-15 \mu m$  in size appear and consist of crystals and particles with a diameter of  $2-3 \mu m$ , then spheroids resembling a single raspberry grain are formed, then trapezoid crystals of base  $3 \mu m$  and height  $1 \mu m$  are observed, and finally, laminated globules consisting of separate iron laminated crystals (LC)  $0.3-0.4 \mu m$  thick are formed (Fig. 6).

Similar compact iron coatings with crystals oriented as parallel strips consisting, in turn, of finer semispheroids are formed upon the decomposition of Fe<sub>5</sub>C(CO)<sub>15</sub>. The further increase in the temperature (to 600-700 °C) of the support covered with a metallic layer formed at lower temperatures induces the growth of laminated iron crystals with an edge length of 3–5 µm and a thickness of 0.3–0.6 µm. At higher temperatures,  $\alpha$ -Fe whiskers grow from the same globules on which the laminated crystals are formed (Figs 7 and 8). This combined growth of laminated whiskers is typical of the decomposition of only



**Fig. 6.** Microphotograph of the surface of an iron coating obtained upon the decomposition of  $Fe_3(CO)_{12}$  at a temperature of the support of 700 °C.

solid iron carbonyls (unlike IPC). As a result, at similar temperatures, a globular crystalline coating with particle sizes of  $25 \times 60 \ \mu m$  is replaced by a purely crystalline layer with pronounced, well formed, and distinctly cut crystals



Fig. 7. Parallel growth of whiskers and laminated crystals from  $Fe_3(CO)_{12}$  vapors at a temperature of the support of 850 °C.



Fig. 8. Growth of whiskers and laminated crystals from  $Fe_5C(CO)_{15}$  vapors at a temperature of the support of 750 °C.

Starting iron carbonyl	T <sub>S</sub> ∕°C	Whiskers		Character of IW and LC		
		l <sub>max</sub> /μm	d/µm			
Fe(CO) <sub>5</sub>	850	_	_	Compact semispherical coating with discrete cupola-like structures $\sim 1 \ \mu m$ in size		
	950	15-20	0.3-0.5	Rectangular IW with "growth steps"		
	1050	60	1—2	IW with distinct cutting, direct and changing growth direction		
	1150	10	4-5	Polycrystals, overgrown structures, absence of IW		
Fe <sub>3</sub> (CO) <sub>12</sub>	700	_	—	LC of Fe of length 10 $\mu$ m, thickness 0.3–0.4 $\mu$ m, and height 5 $\mu$ m		
	800	10-15	0.5–1.0 (at base) 0.2–0.5 (at vertex)	IW of cone type with distinct cutting		
	900	10-15	1.0	IW and LC of thickness 0.3–0.5 um and length 15 um		
	1000	_	_	Isometric single crystals, 3 µm		
$Fe_5C(CO)_{15}$	600	_	_	LC of length 5–6 $\mu$ m and thickness 0.4–0.5 $\mu$ m		
5 . 715	700	10—15	0.5 (at base) 0.2 (at vertex)	IW of cone-type		

 Table 1. Temperature effect on the growth of whiskers and laminated crystals (LC) of Fe obtained from iron carbonyls at 0.15 Torr

*Note:*  $T_{\rm S}$  is the temperature of the support,  $l_{\rm max}$  is the maximum length, and d is the diameter.

with "growth steps" and then by a spheroidal coating with particles virtually equal in size  $(3-4 \mu m)$ . Finally, when the temperature is increased by the next 50 °C, the sublayer surface gains a strongly developed globular crystalline character with the particle size from 5 to 60  $\mu m$ , and these particles are divided into finer cubic crystals, which probably act as nuclei of future IW.

Based on the results of studying the temperature effect on the course of iron carbonyl decomposition in a hightemperature interval and on the growth of IW (Table 1), we can draw the following conclusions.

1. Unlike the formation of metallic films and coatings, the growth of IW occurs in a rather narrow temperature interval ( $\sim$ 50°). This interval is restricted both from the top and bottom, *i.e.*, the temperature plot of the IW growth has a threshold.

2. When the number of metal atoms in the starting iron carbonyls increases, the lower boundary of the temperature "threshold" of IW appearance decreases and the temperature interval of IW formation and growth becomes narrower.

3. The growth of IW occurs in two steps: at first a sublayer is formed and then IW are formed.

4. An increase in the support temperature in an interval of IW formation results in the elongation of the crystals and their apparent diameter (from 10 to 60  $\mu$ m and from 0.5 to 3  $\mu$ m, respectively) and in an increase in their density on the support. The maximum length and density of  $\alpha$ -Fe whiskers fall on a temperature range of 1000–1050 °C. The data on the influence of the partial pressure of iron carbonyls (for IW as an example) on the growth of  $\alpha$ -Fe whiskers at a temperature of the support of 950 °C are presented in Table 2. The following specific features of the growth of IW from IPC can be noted.

1. By analogy to the temperature range, there is a narrow interval of IW vapor pressures in which IW grow. At pressures  $<9 \cdot 10^{-2}$  Torr, IW do not grow and only thin, nonuniform coatings are formed. At pressures exceeding the upper pressure threshold, IW do not appear either but loosen coatings and coatings with laminated crystals or

**Table 2.** Pressure influence on the growth of whiskers of  $\alpha$ -Fe and LC of Fe obtained from Fe(CO)<sub>5</sub> at 950 °C

$\overline{P_{\rm Fe(CO)_5}}$	IW		Character of IW and LC		
/Torr	l <sub>max</sub>	d <sub>max</sub>			
	μm				
$9 \cdot 10^{-2}$	—	_	Nonuniform coating of crystalline type		
$1.5 \cdot 10^{-1}$	15-20	0.3-0.5	Rectangular IW with growth steps, distinctly cut		
5·10 <sup>-1</sup>	30	1.0-1.5	Rectangular IW with a "growth" droplet at the vertex and cone-type IW		
$9 \cdot 10^{-1}$	10-15	2.0-3.0	IW of dendrite type		
1.0	_	_	Fe polycrystals of length 10 μm and diameter 3 μm and dendrites		

irregular structures having secondary aggregates are formed.

2. An increase in the pressure within the interval indicated (as well as the temperature increase) results in the elongation of the IW themselves and their diameter and an increase in the density of IW growth per surface unit.

3. The partial pressure of IPC has a substantial effect on the crystal morphology. Distinctly cut single crystals of  $\alpha$ -Fe with growth steps at the vertex were obtained at the lower limit of the partial pressure interval (Fig. 9, *a*). The pressure increase changes the shape of cylinder-like IW, which become cone-like with a spherical "droplet" at the cone point (see Fig. 5). The crystals appear that exhibit a turn of the IW axis or the beginning of side growth, as well as different surface defects: steps and deflections (Fig. 9, *b*) The further pressure increase results in the growth of branched dendrite-type crystals, the appearance of bridges and polycrystalline forms, and the complete disappearance of IW (Fig. 10).

Effect of support (including the sublayer morphology) on the IW growth. The analysis of electron microscopic





**Fig. 9.** Whiskers of  $\alpha$ -Fe obtained at temperatures of the support of 950 °C (*a*) and 1100 °C (*b*) and an IPC vapor pressure of  $1.5 \cdot 10^{-1}$  Torr.



Fig. 10. Whiskers with secondary formations. The temperature of the support is 1150 °C, and the vapor pressure of IPC is  $9 \cdot 10^{-1}$  Torr.

patterns for many IW samples obtained under different conditions indicates that one should distinguish the effect of the support itself (on which iron carbonyl vapors decompose) and the effect of a metallic sublayer, which is formed directly on the initial support during iron carbonyl decomposition beginning from 200 °C. The formation of this sublayer is a necessary condition for the nucleation and growth of IW. Whiskers grow only on discrete, cupola-like (semispheroidal) structures of the sublayer ~1 µm in size, which we call nuclei. In one of the experiments, we succeeded to detect (Fig. 11) the beginning of growth of a cone-like crystal from this nucleus.

A coating-sublayer is formed on both metallic (stainless steel, steel-3, Nichrome, molybdenum, tungsten, and others) and nonmetallic supports (carbon rods, ceramic tubes). Whiskers grow well on metallic supports, and their modification by donor additives (for example, an eutectic



**Fig. 11.** Beginning of the growth of  $\alpha$ -Fe whiskers on cupolalike (semispherical) structures of the sublayer.



Fig. 12. Formation of whiskers on a support coated with an eutectic FeS alloy at 750 °C.

alloy FeS) results in an additional growth of IW with a higher density on the treated regions. In addition, the growth of the sublayer followed by that of whiskers at a fairly short exposure (~1 min) occurs only on these surface regions. The low-temperature threshold of IW growth decreases (for IPC, to 750 °C), and unusual aggregates consisting of repeating structures (Fig. 12) are observed along with standard whiskers. The unusual aggregates resemble a toroidal pattern of magnetic field lines of force around a magnet. These periodical structures are formed, probably, due to a certain combination of the rate of IPC decomposition on charged centers localized along magnetic field lines of force and the rate of formation of  $\alpha$ -Fe ferromagnetic domains below the Curie point (768 °C).

Effect of electric and magnetic fields on the IW growth. The data indicating the influence of electric and magnetic fields on the length and orientation of IW are published.<sup>8,11,12</sup> Therefore, we studied the influence of a dc electric field on the IW growth within intervals from 200 to 2000 V and from 1 to 10 V. At high electric field values (200-2000 V), IW stopped growing, whereas the change in the electric field from 1 to 10 V had no substantial effect on the IW length.

Additional studies are required to understand the phenomena of parallel crystallization of iron precipitates forming a relief as strips for crystal growth from  $Fe_3(CO)_{12}$  and  $Fe_5C(CO)_{15}$  vapors and the retention of the parallel orientation during laminated crystal growth or the formation of groups of crystals oriented in one direction. It is most likely that these phenomena are related to the ferromagnetic nature of a precipitate.

**ESR spectroscopic study of the thermodissociation of iron carbonyls.** The conditions of ESR spectra recording were close to the conditions of IW preparation *via* the technological scheme used. The data of ESR spectroscopy for IPC are collected in Tables 3 and 4.

**Table 3.** Isotropic values of the g factor for iron carbonyl radical anions (ICRA) detected in experiments on IPC thermal dissociation (183 K)

ICRA	g Factor*
Fe(CO) <sub>4</sub> <sup>•–</sup>	2.0485
$\operatorname{Fe}_2(\operatorname{CO})_8$ -	$\begin{array}{c} (2.0486 \ {}^{26}) \\ 2.0394 \\ (2.0385 \ {}^{27}) \end{array}$
Fe <sub>3</sub> (CO) <sub>11</sub> •-	$(2.0383^{-17})$ 2.0493 $(2.0497^{-27})$
$Fe_3(CO)_{12}$	2.0018 (2.0013 <sup>27</sup> )
$\operatorname{Fe}_4(\operatorname{CO})_{13}$ .	2.0134 (2.0134 <sup>27</sup> )

\* The data in Refs 26 and 27 are presented for the THF and 2-Me-substituted THF solutions at 193 K.

**Table 4.** Anisotropic values of the g factor for iron carbonyl radical anions detected in experiments on IPC thermal dissociation

ICRA	Anis	sotropic va of g factor	<i>T</i> /K	Refs	
	$g_1$	$g_2$	$g_3$		
Fe(CO) <sub>4</sub> <sup>•</sup> -	2.0710	2.0710	2.0038	183	*
	2.0707	2.0707	2.0039	77	28
$Fe_2(CO)_8$ -	2.0566	2.0523	2.0090	183	*
	2.0557	2.0501	2.0094	103	29
	2.0579	2.0538	2.0093	77	30
	2.0540	2.0540	2.0092	77	27
$Fe_3(CO)_{11}$ .	2.0927	2.0314	2.0247	183	*
	2.0921	2.0321	2.0243	77	27
	2.0966	2.0297	2.0253	77	31

\* Data of this work.

In experiments simulating different steps of dissociation (variation of the time and temperature of heating), we detected a family of signals with the *g* factor in an interval of 1.9–2.1 corresponding to iron carbonyl radical anions (ICRA) with the number of iron atoms from one to four. Some groups of the signals (which are not presented in the tables) can be attributed to carbonyl—carbide radicals of the Fe<sub>5</sub>C(CO)<sub>14</sub><sup>•–</sup> type. Depending on the radical anions to surface bond strength, all signals detected can be divided into two groups: with isotropic and anisotropic values of the *g* factor. The rigidly linked ICRA (chemosorbed) give signals with anisotropic *g* factors, and the free (physically adsorbed) ICRA are characterized by isotropic *g* factors.

Prolongation of heating of a sample does not remarkably change the spectra. The only restraint is the growth of the coating thickness, which does not allow the measurement of ESR spectra because of the formation of a magnetic phase that decreases the resonator Q-factor. The repeated recording of the spectra of the same sample, *i.e.*, elongation of the reaction time, either does not result in significant changes in the spectra, indicating the stability of radical ion species (except for the short-lived Fe(CO)<sub>4</sub><sup>•-</sup>) and a high rate of their formation and, hence, a high rate of the IW growth. The temperature increase leads to the broadening of the signals instead of their weakening, which is related to electron exchange reactions in the adsorption layer.

Presently, several approaches are known<sup>8–10,32,33</sup> to explain the thermal dissociation of metal carbonyls in general and under the conditions of IW growth in particular. This is related to the complex character of the reaction under study including different physicochemical steps: evaporation, mass transfer, adsorption, dissociation, formation or growth of IW, and others. Using IPC as an example, let us consider the chemical aspects of the mechanism of metal carbonyl dissociation, *i.e.*, a sequence of elementary acts in the gas phase and on the growing surface, resulting in IW formation.

The thermal dissociation of IPC is usually described as a set of consecutive or single-step decarbonylations<sup>34–36</sup> due to the thermal excitation of molecules with an active involvement of the surface "ad-atoms" in the formation of a crystalline phase. Either intermediates of the Fe(CO)<sub>n</sub> (n = 1-4) type or "naked" Fe atoms incorporate into the lattice. These intermediate species were detected under the hard photolysis of iron carbonyls in inert low-temperature matrices.<sup>37</sup>

The results of studying the IW growth in strong electric and/or magnetic fields<sup>11,12</sup> suggest the formation and participation of charged ions and radical ions<sup>11,38</sup> in crystal thermal dissociation and growth *via* the scheme of successive decarbonylation of metal carbonyls under the conditions of dissociative ionization under electron impact.  $^{12,39}$ 

$$M(CO)_{6} \xrightarrow{-e^{-}} M(CO)_{6}^{+} \xrightarrow{-CO^{+}} M(CO)_{5}^{+} \xrightarrow{-CO^{+}} M(CO)_{4}^{+} \xrightarrow{-CO^{+}} M^{+}$$

M<sup>+</sup> is metal atom.

This approach seems to be quite substantiated, because studies of the behavior of metal carbonyls in reactions with Lewis bases in solutions of different organic solvents<sup>40–43</sup> and of the gas-phase ion-molecular clusterization of metal carbonyls by high-pressure mass spectrometry and ion cyclotron resonance<sup>44–45</sup> showed that these reactions can be considered as radical or radical ion processes with the initiation of primary radical species due to activating complexation and further cluster enlargement.<sup>41–43</sup>

Activating complexation implies the formation of an active (with the properties of a reducing agent with respect to a nonactivated molecule of metal carbonyl) organometallic compound as a result of the reversible addition of a nucleophilic molecule at one of the carbonyl ligands

$$Fe_n(CO)_m + Nu: \implies [Fe_n(CO)_{m-1}C(O)Nu]$$

Nu is nucleophile.

We propose the chain radical ion mechanism of thermal dissociation of metal carbonyls with chain nucleation *via* the scheme of activating complexation, which includes all steps characteristic of chain processes: chain nucleation and the appearance of active iron carbonyl radical anions, chain propagation, enlargement and mutual transformations of ICRA, formation of an  $\alpha$ -iron structure and chain termination, decay of radical ion centers, and cessation of the fast IW growth in length.

The step of chain nucleation begins from the adsorption of an IPC molecule from the gas phase on an adsorption donor site (S) of the starting unchangeable support. These sites are mainly admixtures or formed due to contact of the support with atmosphere. They exist in any supports and interact with an IPC molecule.



[M] are nodes of the crystalline lattice of supports of different nature.

Coordination is usually performed with the participation of one of the carbonyl ligands *via* the hydroxycarbenium type. Chemosorption of this type was demonstrated by the study of the adsorption of carbonyl complexes  $Cr(CO)_6$  and  $C_5H_5Mn(CO)_3$  on metallic surfaces<sup>46,47</sup> and different carbonyls, including iron carbonyls on oxide supports.<sup>48,49</sup>

After adsorption, a radical ion center is nucleated, which determines the radical nature of the process as a whole. Two types of nucleation reactions can be distinguished: (1) on admixture atoms or groups of donor atoms and on the starting support and (2) on the surface of spherical nuclei of a metallic sublayer already formed on the primary support of the metallic sublayer. In both cases, the key role belongs to the one-electron transfer. In the case of initiation on the starting supports, the redox disproportionation of IPC molecules occurs due to electrons of donor sites of the support, due to which reactive species with an open electron shell appear on the surface.



This process occurs at relatively low temperatures. For instance, a metallic (in our case, iron) coating-sublayer, on which chain nucleation occurs in the scheme proposed, is formed at temperatures from 250 °C. In addition, coating formation is characterized by a broad temperature interval (larger than 500 °C) and a high rate of IW growth depending on the concentration of admixture (donor) sites. In fact, the modification of a support of an eutectic Fe-S alloy results in an increase in the density of iron IW on donor sites Fe-S. In addition, at short (~1 min) exposure times, when a cupola-like structure of the sublayer necessary for the IW growth under normal conditions had no time yet to form, an exclusive growth of the sublayer and IW is observed only on the surface regions treated by eutectic. All these data indicate a strong influence of an initiator on the IW growth and profit of donor admixtures.

In the case of chain nucleation on the surface of spherical nuclei of a metallic sublayer already formed on the primary support, the surface group of iron atoms of certain structure and size (~1  $\mu$ m) is an electron donor. To perform the electron transfer to an adsorbate molecule, it is necessary to consume an energy for surmounting a relatively high work function for an electron withdrawal from iron (1.5 eV). This results in a strong temperature dependence of the IW growth and the existence of a lower temperature limit for IW formation, which is much higher than the temperature limit of the beginning of coating formation, as well as the dependence of the nucleus size. Whiskers are formed only on rather large nuclei (~1  $\mu$ m), and IW are completely absent on smaller nuclei. When the temperature increases, high-lying unoccupied electron levels in the conductivity band are populated to provide the electron transfer from a metallic nucleus to an IPC molecule.

$$[Fe_n] \cdots Fe(CO)_5 \longrightarrow [Fe_n]'^+ - Fe(CO)_4^- + CO$$

The formation of discrete structures of rather large size also facilitates the electron transfer due to approaching and flexure of surface electron levels.

The decrease in the temperature of the beginning of IW growth observed in experiments is parallel to a decrease in the electrochemical reduction potential of iron carbonyls in the series

and agrees with the fact that the energy of electron transfer from the metal surface to an adsorbate molecule depends on its electron affinity. It is also clear why the lowtemperature boundary of iron IW growth decreases when hydrogen is introduced into the system (simultaneous inlet of H<sub>2</sub> and IPC),<sup>2,3</sup> because the presence of hydrogen facilitates the reduction of an adsorbate and the step of IW growth initiation.

$$[Fe_n] \cdots Fe(CO)_5 + H_2 \xrightarrow{\Delta} [Fe_n] - HFe(CO)_4^* + CO$$

The formation of radical anions  $Fe(CO)_4$  by the thermal dissociation of iron carbonyls confirms directly redox processes during IW nucleation (see Tables 3 and 4).

A possibility of two types of IW nucleation makes it possible to understand why the induction period exists before the beginning of IW growth and why two steps of the process exist, where at first an iron sublayer is formed and then IW growth begins in this sublayer.

At the step of chain propagation, adsorbed radical anions formed in the previous step react rapidly with neutral iron carbonyl molecules to form a family of iron carbonyl radical ion clusters with different numbers of metal atoms (see Tables 3 and 4).



Additives of small amounts of an inhibitor, for example, ammonia that reacts readily with ICRA, to IPC vapors cease the IW growth, which confirms the chain mechanism of the reaction under study. With the addition of new Fe(CO)<sub>5</sub> molecules and during chain propagation, the rapidly growing core of a cluster gains the structure of an  $\alpha$ -Fe crystal and forms a ready surface unit that can incorporate into the crystalline lattice. It can be assumed that these are  $Fe_4(CO)_{13}$  <sup>-</sup> radical anions (after their complete decarbonylation) that are incorporated due to a similar structure of the [Fe<sub>4</sub>] fragment in the Fe<sub>4</sub>(CO)<sub>13</sub><sup>-</sup> cluster and  $\alpha$ -Fe crystal. In addition, the catalytic Bell-Boudoir reaction resulting in contamination of the metallic surface can occur for heavier clusters, while the IW that formed are characterized by high purity. Thus, in the second step  $\alpha$ -Fe whiskers grow rapidly in length with a rate of 1.5  $\mu$ m s<sup>-1</sup>, which agrees with rather high rates of ICRA clusterization in the liquid  $(10^3 - 10^4 \text{ mol } \text{L}^{-1} \text{ s}^{-1})^{42}$ and gas phases  $(10^{-12} - 10^{-9} \text{ cm}^3 \text{ s}^{-1}).^{44}$ 

The rate of chain propagation reactions should depend on the IPC pressure. In fact, when operating at the lower boundary of an admissible IPC pressure  $(1.5 \cdot 10^{-1} \text{ Torr})$ , the IW length shortens when remoting from the IW growth band from the site of IPC inlet. The IPC concentration also affects the shape of IW. At low partial IPC pressures, neutral molecules come from the gas phase, and a mechanism of the vapor-crystal type occurs when the crystalline surface is formed directly from the gas phase.<sup>52</sup> In this case, perfect crystals with characteristic "growth steps" are formed. At high pressures, the Langmuir-Hinshelwood mechanism (vapor-liquid-crystal) results in crystals with congealed droplets at the vertex in the upper parts of a crystal (see Fig. 5). These droplets represent the liquid phase of polynuclear iron carbonyl clusters.

The last step of thermal decomposition is chain termination ceasing the IW growth. It occurs through the re-



turn of a free electron of ICRA to the conductivity band and is accompanied by the formation of a neutral adsorption complex.

The radical anion adsorption complexes that are chain carriers can decay with a temperature decrease or when additives inducing ICRA "recombination" are added. The inverse electron transfer can occur when the IPC concentration decreases, due to which mononuclear ICRA that nucleated have no time to stabilize because of enlargement. The IW growth becomes impossible but the coatings continue to grow due to admixture nucleation, which is still possible under these conditions.

The temperature effect on the chain termination is also indicated by the existence of an IW growth band  $(40-50 \ \mu\text{m})$  in the direction perpendicular to the support. Longer whiskers grow at an angle to the surface.

Thus, we proposed a model that provides a non-contradictory explanation of the whole array of experimental facts concerning the characteristic features of the composition and morphology of IW and the kinetics of their growth. The model agrees well with the models of chain radical ion processes initiated by activating complexation proposed for the liquid and gas phases.

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