



Kinetics of interaction of tungsten metal with a fluoropolymer

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ABSTRACT

The kinetics of the interaction of tungsten metal with a copolymer of tetrafluoroethylene and vinylidene difluoride (TFE–VDF) has been studied by mass spectrometry (MS), thermogravimetry (TG), and differential scanning calorimetry (DSC). Measurements were taken in a vacuum (MS) and in a dynamic argon atmosphere (DSC, TG) in temperature ranges of 550–585 K (MS) and 313–873 K (TG, DSC). The interaction of tungsten with the fluoropolymer is at least a two-stage process. Its kinetics is described by the Prout–Tompkins *n*th-order autocatalytic equation. It follows from the kinetic dependences and parameters obtained that the rate-limiting stage of the overall process is the formation of the highest tungsten fluoride WF₆.

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1. Introduction

Fluoropolymers are widely used as non-stick, anti-corrosion, and insulating coatings of metals. Unfortunately, most studies dealing with reactions of fluoropolymers with metals are qualitative in character and have not addressed the compositions and amounts of reaction products and the heats and rates of the corresponding reactions. The unique properties of fluoropolymers are mainly due to a rather high carbon–fluorine bond energy of 507 kJ/mol as compared with the common bond energies of 415 kJ/mol for C–H and 348 kJ/mol for C–C [1]. Among the fluoropolymers, polytetrafluoroethylene, which was discovered by Plankett in 1938 [2], is most often used owing to its physicochemical and mechanical properties. Numerous fluoropolymers with different properties are currently known, the differences being due to a different degree of fluorination and branching of the carbon backbone, as well as the presence of substituents in a polymer. Polymers with desired properties are commonly obtained by copolymerization of different monomers taken in various ratios. The monomer units are randomly distributed along the polymer chain. Tetrafluoroethylene and vinylidene difluoride (TFE–VDF) copolymers are widely used as components of anti-corrosion lacquers and coatings.

We have shown [3] that, contrary to the common opinion concerning fluoropolymers, the TFE–VDF copolymer can be a rather aggressive chemical compound under certain conditions so that it can be used as an inert coating on metal surfaces only at temperatures below 533 K. Metals react with fluoropolymers to produce

volatile fluorides, which are hazardous for human health and pose a threat for the technological process as a whole. Study of the reactions of fluoroplastics with metals will make it possible to determine the service conditions and optimize the preparation conditions of coatings on metal surfaces.

In this paper, we report the results of studying the interaction of the TFE–VDF copolymer with tungsten metal.

A system composed of a tungsten powder and a polymer powder was taken as the experimental model. Tungsten was selected on the basis of the following considerations. The reaction of tungsten with the fluoropolymer is accompanied by a considerably lower heat release as compared with the reaction with Ta, Nb, or Ti [3], which prevents the observation of possible features in thermoanalytical curves that can arise from other stages of the process.

Previously [3], we showed that the interaction in the M–F42 system in the temperature range 550–630 K is accompanied by a considerable heat release and a weight loss of 5–35%. Mass spectrometry showed that transition metals react with the fluoropolymer to form their highest fluorides TaF₅, NbF₅, TiF₄, WF₆, and MoF₆ and, in the case of molybdenum and tungsten, oxofluorides WOF₄ and MoOF₄. In addition, the interaction is accompanied by partial destruction of the polymer so that the mass spectra of the gas phase show the ions corresponding to low-molecular-weight hydrocarbons and fluorohydrocarbons.

The presence of the oxofluorides was explained [3] by the presence of water in the initial polymer, which was synthesized in an aqueous medium [4]. ¹H NMR showed that the polymer contains no more than 0.4 mol% (0.1 wt.%) H₂O. Thus, the interaction of a metal with the fluoropolymer involves at least three different processes—formation of a metal fluoride, partial hydrolysis of this fluoride to form oxofluoride, and partial destruction of the polymer, as well as heat and mass transfer processes.

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In this work, the kinetics of the reaction of tungsten with TFE–VDF was studied by thermogravimetry, calorimetry, and high-temperature mass spectrometry.

2. Experimental

The commercially available TFE–VDF copolymer F42 (Russian State Standard GOST 25428–82) containing 21 mol% TFE and 79 mol% VDF was used. A tungsten metal powder was prepared by filing a metal ingot with a diamond file. The average particle size was 80 μm . The W content was 98 mol%.

Samples of metal–polymer composites were molded by hot pressing of mechanical metal–polymer mixtures on a table-top pneumatic press with heated plates (Gibitre Instruments). A rectangular mold, 50 mm \times 10 mm, with a heater was used. The metal and fluoropolymer powders were taken in amounts such that the molar ratio of tungsten to the fluorine in the polymer sample was 1:6. They were placed into the press mold and heated to 423 K; then a load of 200 atm was applied for 5 min, the press mold was cooled to 353 K, the pressure load was removed, and the sample was taken from the mold. The punch and die of the press mold were covered with a Teflon film after each hot pressing event to avoid sticking of samples. The final composite specimen was a plate 50 mm \times 10 mm with a thickness of 1–1.2 mm. From this plate, rectangular specimens 3 mm \times 2 mm were cut for mass spectrometric and calorimetric studies.

Simultaneous TG–DSC was carried out on a NETZSCH STA 449C Jupiter thermoanalyzer equipped with an electromagnetic microbalance with top loading. The TG resolution was 0.1 μg . The relative error of weight determination was 0.5%. A highly sensitive sample carrier with Pt/Pt–Rh thermocouples was used. Measurements were taken in the temperature range 313–873 K under an argon flow (50 ml/min) at a heating rate of 5, 10, 15, and 20 K/min. Sample weights were 10–15 mg. Gold crucibles with lids were used. Before measurements, the chamber with a sample was evacuated and filled with argon (Ar, ≥ 99.993 vol%; water vapor, ≤ 0.0009 vol%).

Calorimetric experiments were carried out on a NETZSCH DSC 204 Phoenix calorimeter in a dynamic argon atmosphere (50 ml/min). Temperatures were calibrated against the melting points of Hg, In, Zn, Bi, and Pb and the temperature of the phase transition in CsCl.

The gaseous reaction products were identified by mass spectrometry on a MS-1301 mass spectrometer. Molybdenum effusion cells with an evaporation/effusion surface area ratio of 600 were used. A sample was placed in a gold crucible. Temperatures were measured with a Pt/Pt–Rh thermocouple and maintained with an accuracy of ± 1 K. The interaction of the fluoropolymer and the metal was studied in the temperature range 550–585 K. Kinetic curves were recorded by monitoring a change in the intensity of the $^{184}\text{WF}_5^+$ ion produced from the WF_6 molecule [3] as a function of time and temperature. The intensity is similar to the reaction rate, i.e., the concentration per unit time. To determine the dependence of concentration on time, the intensities were integrated over time and the resulting values were normalized: $c(t_i)/c(t_{max}) = \alpha_i(t)$. Here, t_{max} is the time when the WF_5^+ ion intensity is zero, i.e., when WF_6 was released and completely removed from the system. The resulting isothermal curves were processed with the Origin program. The kinetic data obtained in the dynamic experiments were processed using Netzsch software.

The Proteus Thermal Analysis program was used for processing the raw TG and DSC curves, determining heats and weight changes, and smoothing and differentiating the curves.

The Thermokinetics program was used for processing kinetic dependences and solving the direct and inverse kinetic problem. There were tried 18 different models. For all models under consideration, a set of statistical criteria of adequacy was used according to the Netzsch procedure. The optimal model was selected on the

basis of the discrepancies between the calculated and experimental values.

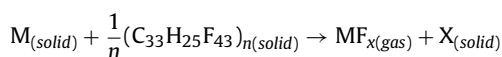
The Peak Separation program was used for decomposing polymodal DSC peaks into components, processing TG curve derivatives, and searching for a best-fit function describing the peak shape.

The DTA/DSC Corrections program was used for recovering the true DSC signal shape, determining the thermal resistance and time constants of the sample-holder system on the basis of reference data (Hg, In, Bi, Pb), and applying corrections to the original DSC curve shape after the determination of heat transfer parameters.

3. Results and discussion

3.1. Mass spectrometry

Thermodynamic analysis showed that the fluorination reactions



involving different metals presumably follow the same mechanism.

Kinetic curves for the formation of WF_6 in the W–F42 system at various temperatures were obtained by mass spectrometry (Fig. 1a and b).

The curves are best fitted by the Prout–Tompkins n th-order autocatalytic equation [5]

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + n \cdot \ln(1 - \alpha) + a \cdot \ln \alpha,$$

where n is the reaction order, and a is the nucleation parameter. The $\alpha = 1$ value in Fig. 1b is the maximum value of the WF_5^+ concentration. For $n = 1$, the kinetic curves in the coordinates of this equation are linearized with $R \geq 0.997$ at $\alpha = 0.2–0.8$, which is evidence that it formally corresponds to the mechanism of the process of the physical model chosen (Fig. 1c). Thus, we determined the kinetic parameters (E/R , n , a) of the reaction for the conversion $\alpha = 0.2–0.8$ and for the entire kinetic range (Table 1).

In this case, E is the activation energy of formation of a mole of tungsten hexafluoride from tungsten metal and the F42 fluoropolymer. In the α range of 0–1, the activation energy is considerably higher than that for α from 0.2 to 0.8 since the former involves energy-consuming stages, such as the induction period, the reaction acceleration onset, and the deceleration of fluorination where diffusion processes are superimposed.

The interaction involves not only the chemical reaction but also mass and heat transfer processes, which can considerably distort the early and late stages. At these stages, the formation of WF_5 is not necessarily the rate-limiting stage. Therefore, the chosen α range 0.2–0.8 corresponds with high probability to the formation of tungsten pentafluoride as the rate-limiting stage.

The autocatalytic character of the reaction is explained by the formation of unsaturated bonds in the carbon backbone of the polymer since some of its fluorine atoms bind to tungsten, which leads to a decrease in the C–F bond energy of neighboring CF_2 groups and an increase in reaction rate [6].

According to the Prout–Tompkins model, solid-state heterogeneous reactions follow a branched mechanism; i.e., cracks and boundary lines along which the reaction propagates are

Table 1
Kinetic characteristics of WF_5^+ formation.

System	α	n	a	$E/R \times 10^3$, K
W–F42	0.2–0.8	1	1	2.0 ± 0.4
	0–1	1.6	0.8	10.0 ± 2.5

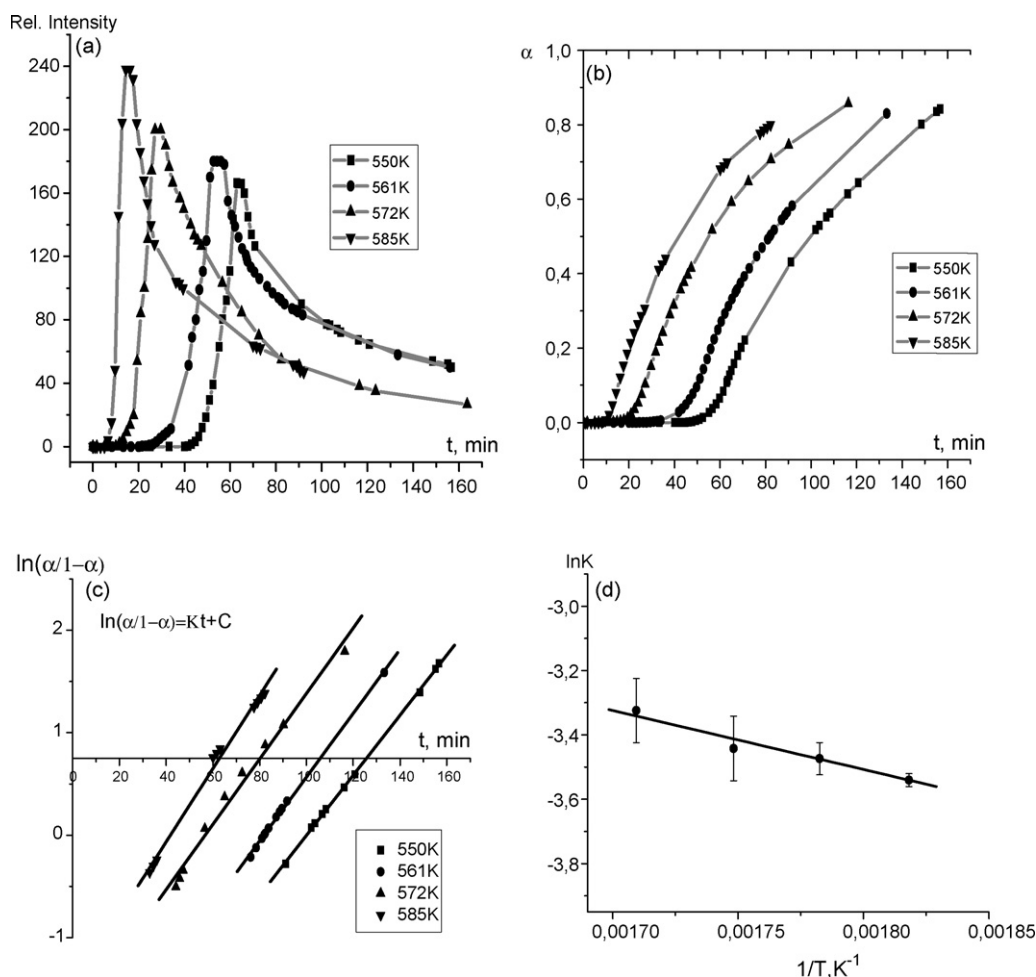


Fig. 1. (a) WF_5^+ formation rate vs. time at different temperatures. (b) Degree of fluorination of a tungsten powder by F42 vs. time at different temperatures. (c) Kinetic data for the fluorination of a tungsten powder by F42 obtained by the Prout–Tompkins equation at different temperatures. (d) Logarithm of the reaction rate constant vs. temperature for a tungsten metal powder.

nonexistent before the reaction onset; rather, they form in the course of reaction, and the probability of termination of chain branching [7] where nuclei are generated is proportional to the conversion.

3.2. Thermogravimetry and calorimetry

Mass spectrometry revealed one stage of the complex processes involved in the interaction of tungsten with the fluoropolymer. To study the process as a whole, we used thermogravimetry and calorimetry. Fig. 2a shows the TG curves for the W–F42 system. The shape of DTG curves is evidence that the process is at least a two-stage one.

The solution of the inverse kinetic problem by the Flynn–Wall–Ozawa (FWO) method [8] with the use of the Thermokinetics program package (Fig. 2c) also showed the existence of two stages.

The first segment of the TG curve (step 1) corresponds to the weight loss $\Delta M = 10\%$ due to the interaction of tungsten with the fluoropolymer, and the second segment (step 2) corresponds to the destruction of the unreacted polymer ($\Delta M = 90\%$). The DTG curve was separated into components with the Peak Separation Program (Fig. 2b). Thus, the entire process can be represented by two successive stages, steps 1 and 2 (peaks 1 and 2 in the DTG curve). Since the model implies a two-stage process, the overlap area S of peaks 1 and 2, which can be an indication of the presence of another stage, was not taken into account. Integration of these stages made it possible to obtain a set of kinetic curves for each stage.

In particular, the solution of the direct kinetic problem for the first segment of the TG data with the use of the FWO calculations as an initial approximation gives $E/R = (5.8 \pm 1.8) \times 10^3$ K, which does not contradict the MS data. The experimental TG curves, as well as the kinetic dependences obtained from the MS data, are reliably ($r \geq 0.998$) described by the Prout–Tompkins n -order equation: at $n = 1.5$, $\log A = 2.3$ and $a = 0.75$.

Fig. 3 shows that the weight loss steps correspond to the endothermic peaks in the DSC curve. The overall endotherm 1 of the interaction of tungsten with the fluoropolymer is caused by a superposition of the exotherm due to the formation of tungsten fluoride and at least two endothermic processes: tungsten fluoride hydrolysis and partial degradation of the polymer chain. Endotherm 2, as already mentioned, is presumably due to the destruction of a polymer excess, i.e., to the C–H, C–F, and C–C bond cleavage.

A series of DTA/DSC experiments was carried out at different heating rates. A functional dependence of the first endotherm was corrected by the DTA/DSC corrections program for recovering the true shape of the DSC signal. Subsequent integration allowed us to obtain and analyze a set of kinetic curves (Fig. 3b). The solution of the direct kinetic problem (the Thermokinetics program) is consistent with the results of TG and MS experiments. The Prout–Tompkins n th-order equation adequately described the experimental dependences: at $n = 1.3$, $\log A = 5$ and $a = 1.1$. The best-fit temperature rate coefficient is $E/R = (5.8 \pm 1.7) \times 10^3$ K. Therefore, step 1 in the TG curve and endotherm 1 in the DSC curve

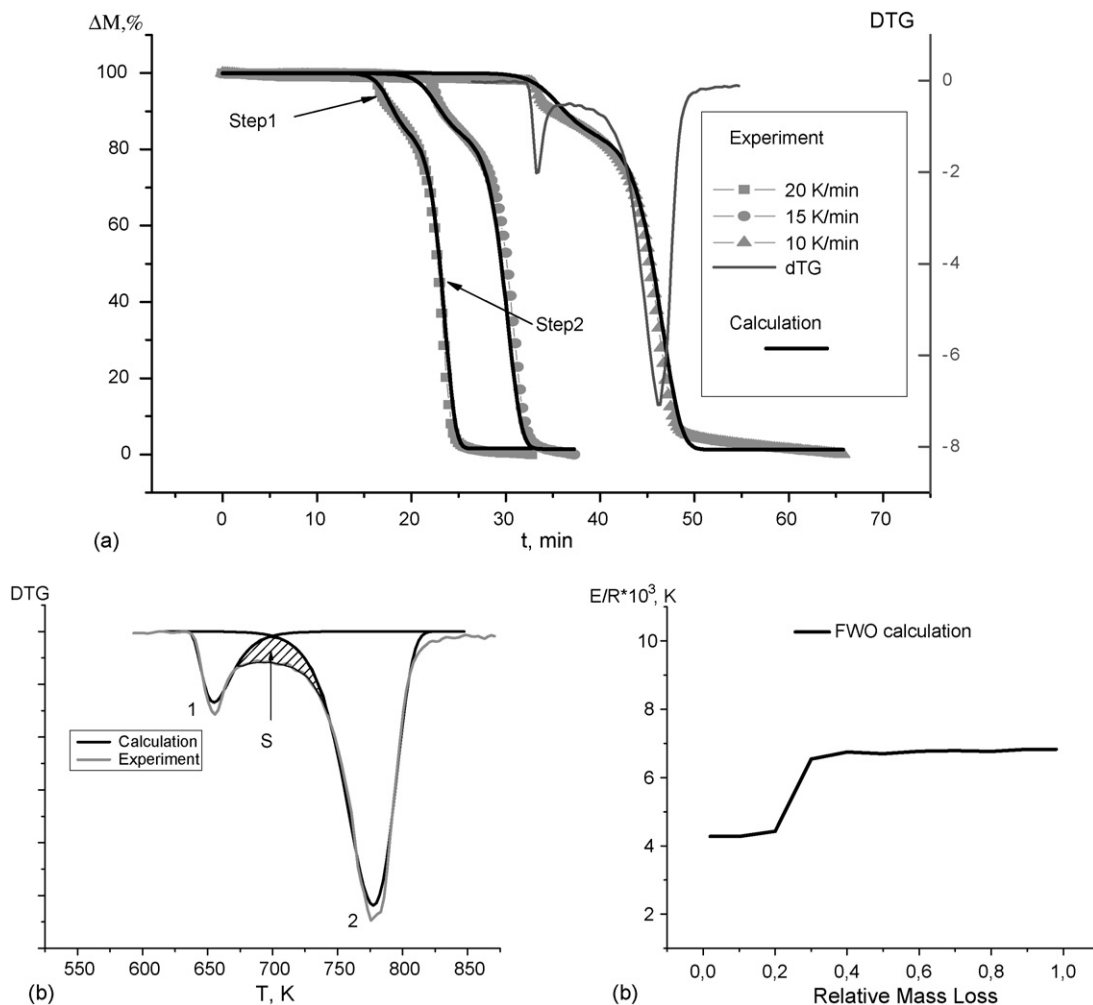


Fig. 2. (a) Experimental and calculated (by solving the inverse kinetic problem) TG curves and the derivative of the TG curve recorded at 10 K/min. (b) Derivative of the experimental TG curve mathematically separated into components. (c) Temperature rate coefficient vs. the extent of reaction.

can be assigned to the same process of formation of tungsten hexafluoride. Step 2 is likely due to decomposition of a polymer excess in the system.

It is worth noting that, as distinct from mass spectrometry, both the TG and DSC curves pertain to the entire process rather than to a

separate reaction stage. Therefore, the consistency of the temperature reaction coefficients obtained for different methods allows us to state that the formation of WF_6 is the rate-limiting stage of the entire process of interaction corresponding to step 1 in the TG curve and peak 1 in the thermoanalytical curve.

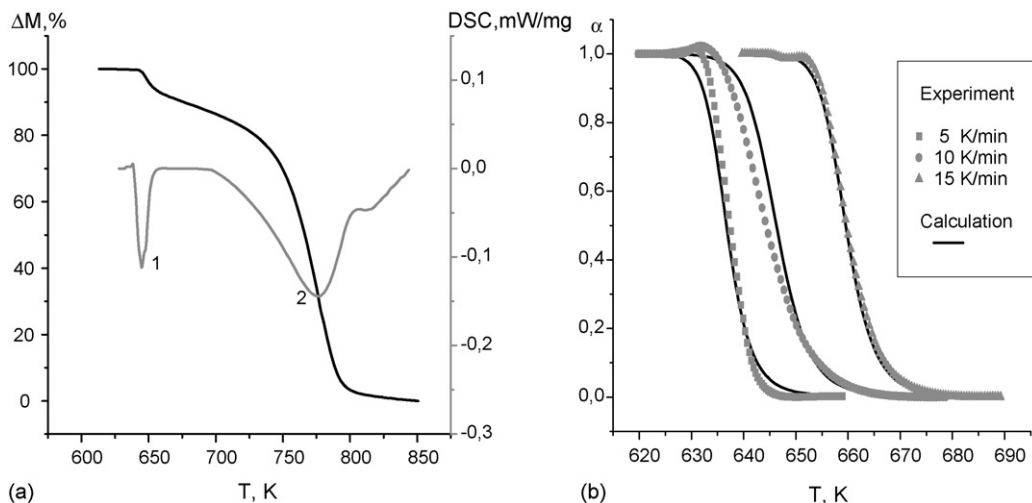


Fig. 3. (a) Simultaneous TG–DSC of the W–F42 system at a heating rate of 10 K/min in an argon atmosphere. (b) Kinetic dependences obtained by processing the DSC curves.

4. Conclusions

The kinetics of the process of formation of tungsten fluoride is characterized by long induction periods and high activation energies in the entire kinetic range. The formation of tungsten fluoride is a rate-limiting stage. On the basis of thermodynamic estimates [3], we can assume that the interaction of F42 with other transition metals proceeds by an analogous mechanism.

The kinetics of this process reflects specific features of the fluorination of d metals with fluoropolymers as fluorinating agents. Whether the interaction is possible depends on the structure of the polymer. The CF₂ groups located between CH₂ groups are first to interact with tungsten [9], which undoubtedly has an effect on the kinetics of the process, especially at early stages.

It is worth noting that fluoropolymeric coatings of metal surfaces are used at considerably lower temperatures than those at which we observed the interaction in the W–F42 system. In many cases, such films are produced by thermobaric treatment. We considered some limiting cases in order to determine the service conditions and optimize the preparation conditions of coatings on metal surfaces. Our findings show that the fluoropolymer reacts

with a metal even at relatively low temperatures. The revealed mechanism of the interaction of the fluoropolymer with metals implies that, even at rather low temperatures, the fluoropolymer can react with a metal to form M–F bonds [10,11], which ensure the adhesion of the fluoropolymer to the metal surface.

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