PHYSICAL CHEMISTRY

Yu. A. LUKYANYCHEV, N. S. NIKOLAEV, I. I. ASTAKHOV,

1962

SovietRxiv

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Fig. 3. 1 –dependence of weight gain on the logarithm of fluorination time at 300°; 2-6 –dependence of the logarithm of weight gain on the logarithm of time for temperatures: 400, 450, 470, 510, 530°

Figure 2: Fig. 3. 1 –dependence of weight gain on the logarithm of fluorination time at 300°; 2-6 –dependence of the logarithm of weight gain on the logarithm of time for temperatures: 400, 450, 470, 510, 530°

Abstract

Full Text

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Yu. A. LUKYANYCHEV, N. S. NIKOLAEV, I. I. ASTAKHOV,
V. I. LUKYANYCHEVA

STUDY OF THE MECHANISM OF COPPER FLUORINATION AT HIGH TEMPERATURES

(Presented by Academician I. P. Tananaev, July 19, 1962)

The study of the process of copper fluorination is of great scientific and practical interest both for investigating the mechanism of the interaction of fluorine with the surface of a metal and for clarifying the conditions of formation and growth of fluoride films of definite structure and properties, in connection with the possibility of using them in the electrical-engineering industry as an insulating material ([1]). However, literature data on the fluorination of compact copper, with the exception of one incomplete study ([2]), are lacking. Most of the available works concern the study of the fluorination process of copper powder ([3]), its salts ([4]), or a very thin deposited copper film ([5]) (up to 500 Å).

Fig. 1. Growth curves for a copper fluoride film as a function of time at different temperatures: 1 –300°; 2 –400°; 3 –450°; 4 –470°; 5 –510°; 6 –530°.

Fig. 3. 1 –dependence of weight gain on the logarithm of fluorination time at 300°; 2-6 –dependence of the logarithm of weight gain on the logarithm of time for temperatures: 400, 450, 470, 510, 530°.

In the present work the process of copper fluorination on compact metal was studied in the temperature interval 300-600° in a dynamic apparatus at atmo-

spheric fluorine pressure. The structure and thickness of the films were determined as a function of the fluorination temperature. The phases formed were investigated by X-ray diffraction and electron-microscopic methods. X-ray structural investigations were carried out on an apparatus with ionization recording, URS50-I; electron-microscopic investigations were carried out on a UEM-100 microscope using the carbon-replica method. The chemical composition of the phases was characterized by the fluorine content. Fluorine was determined by the pyrohydrolytic method ([6]). It was established that the fluorine content corresponds to the amount of fluorine consumed in the process of formation

Fig. 2. Electron-microscopic photograph of a fluoride film from copper: a — 300°; b —400°; c —470°; d —510°

fluoride film. Fluorination was carried out in a nickel reactor as follows. Copper plates (purity 99.9%) with a surface area of 25–30 cm^2 were heated in a nitrogen atmosphere to the specified temperature; upon reaching this temperature the reactor was filled with fluorine. The fluorine was obtained electrolytically and purified from hydrogen fluoride impurity with liquid nitrogen and sodium fluoride. Film growth was monitored by the gravimetric method.

Figure 1 presents a diagram of the rate of fluorination of copper at various temperatures. With increasing temperature, the fluorination rate and the film thickness increase. X-ray patterns of the fluoride film obtained on specimens at different temperatures show the formation of only one phase in the temperature range studied—copper difluoride. The thickness of the CuF_2 film in this temperature range increases from ~ 0.7 to 7μ. Electron-microscopic studies show that the fluoride film formed at a temperature of 300° consists of small ($\sim 0.2\mu$), closely intergrown crystals (Fig. 2a) and adheres firmly to the copper surface. The reaction kinetics at this temperature obey a logarithmic law, as is seen from Fig. 3, 1.

The phase formed at higher temperatures consists of larger (at 500°, up to 10μ), well-formed crystals (Fig. 2 b, c, d). In this case the film is characterized by brittleness and in some cases is easily separated from the base metal. This can be explained by the fact that, during the growth of large CuF_2 crystals as a result of recrystallization, the bond between the fluoride film and the metallic substrate is completely lost. Investigation at these temperatures showed that the kinetic curves for different temperatures in logarithmic coordinates fit straight lines well, which corresponds to a simple dependence for the film-growth rate $y^n = kt$. The tangent of the angle of inclination of the straight lines on the indicated diagram changes monotonically from 0.45 to 0.36, which indicates a change in the value of n from 2 (quadratic parabola) to 3 (cubic parabola). The established laws of fluoride-film growth made it possible to calculate the rate constants of the fluorination process as a function of temperature:

Fig. 4. Dependence of the logarithm of the rate of fluorination of copper on the value $1/T$.

τ, °C	K_p
300	$5.6 \cdot 10^{-2}$ mg · cm^{-2} · min^{-1}
400	$7.5 \cdot 10^{-4}$ mg^2 · cm^{-4} · min^{-1}
450	$1.6 \cdot 10^{-3}$ mg^2 · cm^{-4} · min^{-1}
470	$2.2 \cdot 10^{-3}$ mg^2 · cm^{-4} · min^{-1}
510	$6.0 \cdot 10^{-3}$ mg^3 · cm^{-6} · min^{-1}
530	$8.0 \cdot 10^{-3}$ mg · cm^{-6} · min^{-1}

The activation energy of the process of fluorination of copper at temperatures above 300°, calculated from the temperature dependence of the fluorination rate constants (Fig. 4), proved to be 17.9 kcal/mole.

Thus, the process of fluorination of copper as a function of temperature can be divided into two intervals. At 300° the fluorination rate obeys a logarithmic law, as is seen from Fig. 3, 1. An analogous dependence of the fluorination rate was obtained by Brown et al. ([3]) on copper powder at temperatures below 300°. The mechanism of copper fluorination whose rate obeys a logarithmic law is at present difficult to explain. The Mott-Cabrera theory ([7]) explains logarith-

law to a quantum-mechanical transition (tunnel effect). However, this is valid for very thin films.

A satisfactory explanation of the logarithmic law for thick films was given by Evans ([8,9]), who proceeds from the assumption of a mechanical change in the film during the growth process: the film becomes compacted, and diffusion of the gas to the metal surface is impeded. In the case of the formation of a fluoride film with a thickness of $\sim$ 7000 Å, the logarithmic growth law can be explained both by deterioration of the electronic conductivity of the film and by mechanical defects in the film.

Above 300° the mechanism of fluorination is reduced to a diffusion process; the rate-determining stage of the process is the diffusion of the reactants through the film. The change in the exponent n with increasing temperature is associated with an increase in film thickness and a slowing of diffusion.

X-ray phase studies show that at all temperatures only copper(II) fluoride is formed; no other copper compounds were found.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

Received
22 VI 1962

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Note: Figure translations are in progress. See original paper for figures.