Study of Oxide Crystals Growth on Refractory Metals Surface

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Transition metal oxides are widely used as catalysts, besides they are considered to be applicable in solar industry, microelectronics and other modern technologies. So development of effective methods of metal oxides production is subject of extensive investigations.

So this study is aimed at main characteristics (growth rate and mechanism) of oxide microcrystals formation on molybdenum and tungsten filaments during high temperature oxidation. Tungsten and molybdenum oxides exhibit unique physico-chemical properties: gasochromism, electrochromism and photocromism. So they are promising materials for electrochromic displays, gas sensors, smart windows and other applications.

To study oxides structures on the surface of refractory metals we developed an experimental setup based on “hot filament” method. This method consists in a controllable heating of metal filament in oxidizing atmosphere at a gas temperature $T_g$ [1, 2]. The oxides growth is registered by videomicroscopy. Changes of crystal’s dimensions are defined by image processing routine, then their growth rate is calculated.

In so way the mechanisms of oxide layers development are defined on the surface of tungsten and molybdenum filaments heated electrically. It is found that from the beginning a primary oxide film is formed on a tungsten surface. Then numerous whiskers appear above the oxide layer mainly along cracks. Gradually they transform into branched bush-like structures due to prismatic facets overgrowth (Fig.1).

![Figure 1. Bush-like oxide structures on the surface of tungsten filament.](image)

Oxide structures on molybdenum filament appear in the form of microplates, which are oriented in different directions. With time they interconnect and grow together [3]. It is found that the first tungsten oxide whiskers appear at 900 K, whereas molybdenum oxide plates are observed starting with temperature 800 K, because molybdenum oxides are more volatile.
By computer processing successive images of oxides structures we defined their growth rates, depending on growth direction. So for tungsten oxide rate of growth in height (outwards the filament) is distinctly less than growth rate in width – parallel to the filament surface (Fig. 2).

Figure 2. Crystal’s dimensions histories: 1 – crystal height (h); 2 – crystal width (l).

Growth rates for tungsten oxides crystals varies in ranges: in height – 0.1–0.5 mcm/c and in width – 0.1–0.8 mcm/c. As to molybdenum oxide crystals – they increased with equals rates in height and in width: from 0.2 mcm/c up to 0.55 mcm/c for different crystals.

To clarify oxide crystals formation mechanism we fulfilled x-ray analysis of filaments. It was found substantial quantity of carbon on the tungsten surface, possibly as a result of graphite lubricant use during wire-drawing. After thorough surface peeling the whiskers are not formed under heating. So we conclude that the carbonaceous particles are perhaps the centers of oxide vapors condensation.