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LIMITING STAGE OF TUNGSTEN ANODIC OXIDATION ON THE BOUNDARY OF MOLTEN METAL AND SLAG

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The kinetics of anodic oxidation of tungsten on the boundary of oxidic and metallic melts has been investigated.Dependence of density of anodic current on polarization was obtained by using galvanostatic scheme. Slags with the oxides of silicon,calcium,aluminium and magnesium in the base were used as electrolyte.The experiments were carried out at the temperature 1823-1923K.The investigated alloy of iron-tungsten containing 1...6mass % of tungsten was taken as anode;tungsten spiral was taken as cathode and electrode of comparison.The relationship i-η referred to the process $W^{\circ} \rightarrow W^{n+} + ne$ is indicative of the presence of utmost current (i_p). The relationship between density and polarization is well explained by the equation [1] :

$$i = i_p \sqrt{1 + \frac{1}{p} exp\left(\frac{n(p+1)}{\gamma RT} \eta_p\right) - \frac{p+1}{p} exp\left(\frac{nF}{\gamma RT} \eta_p\right)}, \quad (1)$$

where i_p -utmost current of the reaction; n -the number of electrodes in summary electrodic stage; p -summary order of reaction; γ -stoichiometric coefficient; η_p -chemical polarization.

All this allowed to conclude that one of the chemical reactions following the electrodic stage and taking place in thin reactional layer of oxidic melt appears to be a stage which limits oxidation of tungsten.

The laws of stages which precede the delayed stage and take 10^{-6}-10^{-5}c to proceed have been investigated by coulomb-static method.Combined analysis of the investigation results of limiting and quick stages of the process allowed to suggest the following mechanism for anodic oxidation of tungsten:

1) electrodic stage : $W^{\circ} \rightarrow W^{4+} + 4e$; (2)

2) reaction $W^{6+} + 4O^{2-} \rightarrow WO_4^{2-}$ (3) which forms elementary complexes of tungsten.

In accordance with the suggested mechanism of the process,the following equation is derived:

$$i_p = 1{,}63 \cdot 10^5 [W]^{0,8} (WO_3)^{-3} exp\left(-\frac{27680}{T}\right), \quad (4)$$

which connects utmost current value with the temperature and concentrations of tungsten in metal and slag.

Reference
1) K.J.Vetter:Electrohimitsheskaja kinetika,Himija,Moskow,1967,270.