The influence of passivation and adsorption phenomena on the mechanism of electrode processes of some metals (Cu, Pt, Nb, Ta, Ti, W) in low-temperature carbamide-containing melts

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The electrochemical dissolution of metals in carbamide melt and carbamide-containing melts is often accompanied by the passivation of metals. Such metals as Nb, Ta, Ti, W are passivated in carbamide- containing melts, but the degree of passivation of these metals is different. The electroactivity decreases in the order Ti¿Nb¿Ta; it depends on the chemical and physicochemical properties of the passive film (Auger spectroscopy method). The melts containing NH4+ ions possess special properties. In the case of electrode (Pt, Nb, Ta, Ti, W) polarization, the fact is very essential that a chemically active compound possessing depassivating properties is formed in the positive-potential (¿1V) range (in the chloride melt NCl3). The electrodissolution of Ta and Nb is only possible when this compound is involved, its concentration for Ta dissolution having to be 2-3 times higher than for Nb. The dissolution of Ti and W is accompanied by passivation, but the depassivating action of Cl- ions is sufficient for the dissolution of the metals. In fluoride- containing melts, the depassivating agent in the dissolution of all metals is the F- ion. After anodic dissolution, the metals transfer to the melt as ions in the highest oxidation state and form complexes of different composition and structure with melt components (spectroscopic methods). The reduction of the ions of metals formed at electrodes made of these metals proceeds in accordance with their passivating properties: the reduction of Ta(V) ions was not observed at all; Nb(V) ions are reduced to Nb(IV); Ti(IV) and W(VI) ions are reduced to metal (cyclic voltammetry method). However, Ti and W deposits contain no more than 20the rest is oxycompounds. We failed to observe cathodic metal deposition processes at inert (Pt, glassy carbon) electrodes, except the case of reduction of metal ions from an iodide-containing melt at a smooth, glassy-carbon electrode; this is accounted for by the competitive adsorption of melt components on the electrode surface. Platinum and copper are not passivated in carbamide-containing melts. Their electrodissolution and reduction of ions to metal involve no kinetic hindrances.

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