Electrodeposition, Separation and Treatment of Refractory Metals in Some Low - Temperature Melts

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In recent years, there has been a noticeable increase in the interest of researchers in the development of novel low-temperature and room-temperature molten compositions (LTMC) based on organic compounds. Some low-temperature melts have been investigated in our laboratory. These LTMC's may be divided conventionally into two main series, namely protic and aprotic solvents.

The first series includes carbamide-, acetamide-, imidazole -containing melts. Ionic conductivity in these systems is created by addition of NH_4Cl. The electrochemical behaviour of refractory metals (Pt, Pd, W, Ti, Nb, Ta, Cu, Ag, Ni) has been studied and made it possible to make some decisions.

In carbamide-chloride melt ($t_{work} = 120^0C$) a correlation between passivation effects and the mechanism of cathodic processes has been established on the basis of experimental results obtained. During the electrochemical dissolution of the metals that are not passivated (Pt, Pd) (in the presence of complex compounds of Pt chlorides), ammonia chloride complexes are formed, which are discharged at the cathode to deposit pure metals. In the case of weak passivation of electrodes (W, Ti), the electrochemical dissolution of the metals involves formation of carbamide complexes of metals, the reduction of which to metal proceeds stepwise via the formation of intermediates. The cathodic deposit consists mainly of oxychloride compounds of metals in the lowest oxidation state and negligible quantaties of pure metals. The electrochemical dissolution of the metals that are characterized by a strong passivation (Nb, Ta) involves formation of chloride complexes of ions in the highest oxidation state, the reduction of which either does not take place at all (Ta(V), or a recharge of metal ions (Nb(V) → Nb(IV)). Therefore, the obtaining of some cathode deposits is ruled out in this particular case.

In acetamide- NH_4Cl ($t_{work} = 68^0C$) and in acetamide-carbamide -NH_4Cl ($t_{work} = 40^0C$) melts the electrochemical behaviour of refractory metals is the same as in carbamide-chloride melt, but passivation of metals is stronger.

In imidazole- NH_4Cl_($t_{work} = 57^0C$) and in imidazole-indole- NH_4Cl ($t_{work} = 32^0C$), copper and silver dissolved without passivation, and their ions are discharged at the cathode to deposit pure metals, but only a single step corresponding to Ta(V)→Ta(IV) and Nb(V)→Nb(IV) transfers was recorded in previous investigations.

Comparing the results of the investigation of the mechanism of refractory metals electrode processes it is possible to come to the conclusion that the melts of the first group can be used to obtain pure metals in the form of powders (Pt) or electrodeposits (Pt, Ag, Cu) if the metals are not passivated and for electrochemical treatment and surface polishing in the case of metal surface passivation (Ti, Nb, Ta).

The second group of melts includes imidazolinium and quaternary ammonium salts. In 1methyl-3-ethyl imidazolinium chloride only processes corresponding to Ta(V)→Ta(IV) and Nb(V)→Nb(IV) were observed. In tetraalkylammonium chloride, containing $AlCl_3$ a stepwise reduction of $TaCl_5$ was observed, and Ta-Al alloys were obtained on Pt electrode.

We think that this type of salts is more suitable for deposition of pure metals, but it is impossible to use the first group of melts for this purpose because cathodic processes in melts containing NH_4Cl are limited by of hydrogen evolution potential.