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STIMULATION OF RARE METALS DISMUTATION REACTIONS IN CHLORIDE MELTS BY F-ION

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Transition elements of IV and V groups have tendency to form the low-valent ions in chloride melts which determines the instability of redox equilibria in these media used for inogranic synthesis and rare metals electrodeposition. We have established that injection of a stronger ligand, e.g. fluoride-ion, into chloride melts containing Ti, Zr, Hf, Nb, Ta in a divalent state is stimulating the dismutation reaction: $mMe^{n+} \rightarrow nMe^{m+} + Me$ (where $m > n$) at the expense of formation of stable fluoride complexes. The stoichiometry of substitution reaction when chlorine is being substituted by fluorine in ion shells of transition metal central atoms, have been determined by linear-sweep voltametry and amperometric titration methods:

$3Me\,Cl_2 + 12F^- = 2Me\,F_6^{3-} + Me + 6Cl^-$ (for Ti),
$2Me\,Cl_2 + 6F^- = Me\,F_6^{2-} + Me + 4Cl^-$ (for Zr, Hf, Nb),
$5Me\,Cl_2 + 14F^- = 2Me\,F_7^{2-} + 3Me + 10Cl^-$ (for Ta)

Formation of the high oxidation state fluoride complexes in the chloride-fluoride melt is typical for zirconium, hafnium and tantalum as the low- and medium-valtent complexes in these cases are not thermodynamically stable. The situation is inverse to titanium and niobium. The equilibrium of dismutation reactions is shifted to the right.