

HAFNIUM IN MOLTEN SALTS: ELECTROCHEMISTRY, CHEMISTRY, ELECTRODEPOSITION

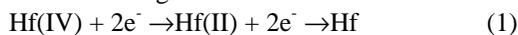
S.A. Kuznetsov, S.V. Kuznetsova

Institute of Chemistry KSC RAS,
14 Fersman Str., Apatity, 184200, Murmansk region,
Russia

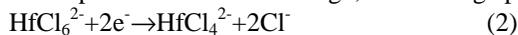
The advanced materials on the base of hafnium can be obtained by hafnium electrodeposition from molten salts.

Electrode processes

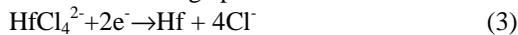
Electrode processes during electrodeposition of hafnium from halide melts were studied. It was found that hafnium cathodic reduction in NaCl-KCl-HfCl₄ electrolyte within the temperature range 973-1173 K involves two successive stages



The recharge process at sweep rate $v < 0,6 \text{Vs}^{-1}$ and $\text{HfCl}_4 \geq 6,1 \cdot 10^{-5} \text{ mol cm}^{-3}$ concentration has been proved to be complicated by the reaction of disproportionation [1]. When polarization rates are high, the recharge process

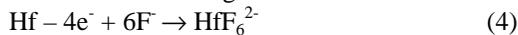


is reversible, with soluble product formation in the melt, while the discharge process



is irreversible [2]. At the same time in the CsCl melt the reduction of the complexes to metal occurs in a single irreversible four electrons stage [3]. The fluoride complexes of Hf(IV) in alkali chloride melts discharge to metal in one irreversible step also [4]. It was shown that the increasing of the melts basicity due to change of composition the first or the second coordination spheres leads to decreasing of diffusion coefficients and heterogeneous charge transfer rate constants for hafnium complexes. During anodic dissolution of hafnium in pure chloride melts the salt passivation of hafnium anode by K₂HfCl₆ compound was found at high anodic current densities in temperature range 973 – 1023 K. The resistance of salt film was calculated on the base of chronoamperometry data.

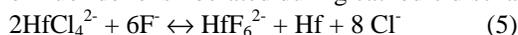
It has been shown [5] that at a low anodic current densities (up to 0.02 A cm⁻²) the mean valence of hafnium is close to four in the melt NaCl-KCl-K₂HfF₆ (10 w/o). This is due to the fact that this current density is not above the limiting diffusion current density for hafnium dissolution according to reaction:



At current densities higher than the limiting diffusion current of the process (4) hafnium dissolves also in the form of HfCl₄²⁻ complexes

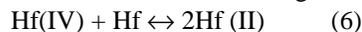
Chemical reactions

The formation of hafnium complexes of different oxidation states during anodic dissolution is an undesirable effect in the melts of a heteroligand composition. Disproportionation reaction will occur in the bulk and at the melt surface on account of the convection of fluoride ions liberated during cathodic discharge:



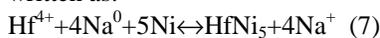
and a film is formed and grow on the melt surface during electrolysis. Film formation reduces the cathodic current efficiency of metal in the form of coherent coatings.

The presence of Hf (IV) complexes in the chloride melts and their reaction with the coating



causes smoothing of the cathodic deposit and has the controlling influence on the retention of planar crystallization front.

Using the NaCl-KCl-K₂HfF₆ (10 w/o) – NaF (10 w/o) electrolyte in contact with hafnium the intermetallic compounds HfNi₅, HfCo₆ and HfFe₂ were obtained on different substrates of Ni, Co and Fe. The formation, for example, of intermetallic compound HfNi₅ can be written as:



The transfer of electrons in this case is carried out by alkali metals, which dissolved in the melt.

Electrodeposition

The effect of anionic, cationic composition of melts, cathodic current density, temperature on hafnium coatings roughness was established.

Different compounds of hafnium such as: hafnium diboride, hafnium-niobium and hafnium-copper alloys, silicides of hafnium were obtained by electrochemical synthesis.

The fields of application of the hafnium and composite materials on the base of hafnium obtained from molten salts were shown.

References

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