Electrocryrstallization from Molten Salts: Effect Analogous to High Pressure Action

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The comparison crystallochemical studies of substances obtained by electrolysis of molten salts and other methods were carried out. Several peculiarities of the structure formation when used the electrodeposition were revealed. Products of cathode electrowrystallization from various complex halide and oxohalide molten systems containing Nb- and Ta-species were subjects of our present investigation.

We observed, among other things, following phenomena. It was found, in particular, that the maximum concentration of oxygen in cubic solid solutions of composition NbO, which were prepared by the electrolysis of molten salts at 720 - 850°C (up to 17 at. %, i.e. up to the composition NbO_{17}), is many times higher than all known concentrations for solid solutions obtained by heating niobium in air (0.5-1.5 at. % at 700-800°C and no higher than 7 at. % at 1700°C) [1,2]. Considering that the external pressure should increase the solubility of oxygen in niobium, it can be concluded that electrowrystalzation of NbO, solid solutions on the cathode exerts an effect analogous to that which appears under high external pressure. This conclusion is supported by the results of our X-ray diffraction investigation. Thus, oxygen atoms in crystals prepared by the electrolytic method are located in the tetrahedral cavities of the bcc Nb structure, whose volume is four times smaller than the volume of octahedral cavities occupied by oxygen upon surface oxidation. In addition, the volume of the cubic unit cell of the crystal of composition NbO_{0.15} which was prepared by the electrodeposition (36.2 Å³) is 4.3% smaller than the volume of the tetragonally distorted unit cell of suboxide NbO (37.78 Å³) [3] of virtually the same composition (NbO_{0.145}).

The conclusion that cathode electrowrystalzation exerts an effect analogous to the rise in the external pressure can also be made based on an analysis of the characteristic features of the tetragonal modification of tantalum (β-Ta) [4]. This phase is a true creation of the electrodeposition from molten salts: single crystals of β-Ta can only be obtained using the electrolytic method (all other metallurgical techniques produce only thermodynamically equilibrium α-Ta with a simple body-centred crystal lattice). The structure of β-Ta is closely related to the recently established structures of high pressure phases of Rb, Cs, Ba, Sr, Bi and Sb [5-7]. The main characteristics of such structures are the extremely short interatomic distances between the channel atoms and the presence of some additional intercalated atoms between the main channel atoms (a local increase of the

of the perovskite-like cubic bronze KTa_{12}O_3 [8] and in the hexagonal bronze K_6Ta_{6+6}O_{15+1}F_{6+6} [9] both produced by electrodeposition from oxygen-containing melts. Approximately 2% of K atoms located in the hexagonal channels of the KTa_{12}O_3 structure are statistically substituted by Ta-Ta dumb bells. An intercalation of additional Ta atoms ~ 2.0 Å distant from the main K atoms and the substitution of one Ta atom by Ta-Ta dumbbell were observed in the large hexagonal channels of the K_6Ta_{6+6}O_{15+1}F_{6+6} structure. As this take place, the X-ray density of the hexagonal bronze (d_{oex} = 5.46 g/cm²) obtained by electrochemical method is noticeably higher than the X-ray density of its isostructural analog K_6Ta_{6+6}O_{15}F_{6+6} obtained by high-temperature sintering (d_{oex} = 5.06 g/cm²).

It is suggested that the local increase of the space filling in the channels and holes is due to the specific conditions used for the phase formation in both β-Ta and the Ta-bronzes (high temperature, electrical field which provides a negative charge of the crystallization surface on the cathode and reducing conditions).

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References