

## **PASSIVATION AND RED-OX PROCESSES OF REFRACTORY METALS IN CARBAMIDE- CHLORIDE MELT**

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### **Abstract**

*The electrochemical behavior of refractory metals (Pt, Pd, W, Ti, Nb, Ta) in the low-temperature carbamide–NH<sub>4</sub>Cl melt ( $t_{\text{exp}}=120\text{ }^{\circ}\text{C}$ ) and the structure of complex ions formed after anodic dissolution have been studied by cyclic voltammetry and spectroscopic methods. The features of the mechanism of metal electrodisolution and possibilities of the cathodic reduction of complexes formed in the melt are presented.*

*A possible correlation between passivation processes on the metal surface, the mechanism of electrodisolution, composition of complexes and the electrochemical activity of metals and their ions are discussed. The data obtained reflect the possibilities to use the carbamide–NH<sub>4</sub>Cl melt for practical purposes - in electroplating and electropolishing.*

*Keywords:* low-temperature melt, refractory metals, electrochemistry, passivation

### **1. Introduction**

The interest in carbamide-based molten mixture is due to its low melting point, its ability to dissolve many salts, ready availability and low cost, which is important in practice. Pure carbamide is not often used for investigation [1-4] because long operation and especially overheating ( $>150\text{ }^{\circ}\text{C}$ ) lead to the polymerization and solidification of the melt. However, by adding to molten carbamide salts, whose ions form strong hydrogen

bonds with carbamide molecules [5], it is possible to retard thermal destruction, and the carbamide-halide mixture becomes stable in time and suitable for long operation. The electrochemical properties of refractory metals, the equilibrium of metals with their ions in high-temperature fluoride, chloride and chloride-fluoride melts are fairly well studied [6-20, etc.]. However, we failed to find literature data on the anodic dissolution of refractory metals in carbamide-containing melts except in our articles [21-23].

The investigation of the electrochemical behavior of the carbamide- $NH_4Cl$  melt at an inert electrode showed that the main cathodic process is the discharge of ammonium ion. Two processes are observed in the anodic part of polarization curves: the first corresponds to carbamide oxidation and the second one - to the oxidation of  $Cl^-$  [24]. At potentials higher than the  $Cl^-$  oxidation potential a new product - the interaction product of  $NH_4^+$ , carbamide and  $Cl_2$  - is formed. This is the case only in a  $NH_4^+$ -containing melt, and the product can be identified by the IR spectra of anodic gases and of the melt at  $630\text{ cm}^{-1}$ . Our experimental data on the electrochemical behavior of some refractory metals in the carbamide- $NH_4Cl$  melt have already been published [21-23]. In this work, new data on the electrochemistry of other metals in this melt are presented. But the main aim of this work is to analyze all the data obtained.

## 2. Experimental

The electrochemical study of the anodic behavior of metals in the carbamide-ammonium chloride melt was conducted by recording cyclic voltammograms with a PI-50-1 potentiostat. A metal electrode with an active surface area of  $5.8 \times 10^{-3}\text{ cm}^2$  was used as the working electrode. The auxiliary electrode was a platinum plate. The potential was measured against silver reference electrode ( $Ag/\text{carbamide} + NH_4NO_3$  (16 mol. %) +  $0.07\text{ mol kg}^{-1} AgNO_3$ ). Experiments were carried out in the temperature range 120 to 140 °C under argon. The state of metal ions in the  $CO(NH_2)_2-NH_4Cl$  (16.8 mol. %) melt was investigated by spectroscopic methods in the temperature range 120-140 °C. UV/VIS spectra were taken during the anodic ( $j_a=5$  to  $150\text{ mA/cm}^2$ ) dissolution of metals with Specord UV/VIS and IKS-14 spectrophotometers adapted for high-temperature measurements. The valency of metal ions formed in the melts during anodic dissolution was determined from the spectra and also gravimetrically. Reagent grade salts and dried argon were used in the study. The salts were pre-dried in vacuum at 80 °C.

## 3. Results

The investigation of the electrochemical behavior of refractory metals ( $Pt$ ,  $Pd$ ,  $W$ ,  $Ti$ ,  $Nb$ ,  $Ta$ ) in the carbamide- $NH_4Cl$  melt ( $t_{exp}=120\text{ °C}$ ) and the spectroscopic study of complex formation of metal ions being in the melt after electrochemical dissolution with

melt constituents allowed us to divide the metals investigated into three groups according to main characteristics.

**Group I.** Metals that are not passivated in the melt (*Pt*, *Pd*). Platinum is electrochemically insoluble in the carbamide and carbamide- $NH_4Cl$  melts. According to the results of investigation of the melt and anode gases composition [24], the wave appearing in the anodic curve in the carbamide- $NH_4Cl$  melt at *Pt* and glassy carbon electrodes (Fig. 1) corresponds to the anodic oxidation of carbamide. The electrochemical dissolution of *Pt* takes place only if the carbamide- $NH_4Cl$  melt contains corresponding complex salts:  $K_2PtCl_6$ ,  $K_2PtCl_4$  [25]. These salts form ammonia complexes after being dissolved in the melt. The metal ions are electroreduced reversibly to metal (Fig. 2), which is corroborated by the results of X-ray phase analysis of the deposits obtained. In the case of electrochemical dissolution in the carbamide- $NH_4Cl$  melt, platinum forms complexes of different structure with ammonia chloride, and the *Cl* content of the complexes increases during electrolysis.

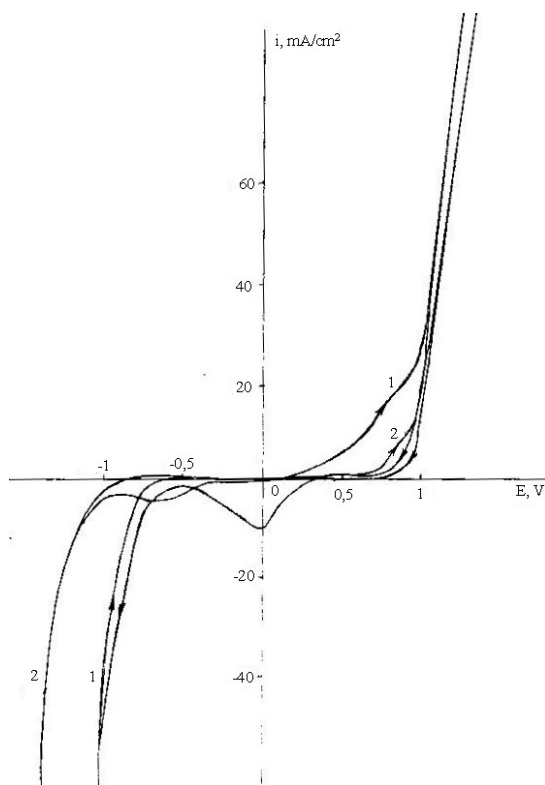


Figure 1. Cyclic voltammogram of Pt(1) and glassy carbon(2) electrodes in the carbamide- $NH_4Cl$  melt,  $t=130\text{ }^{\circ}C$ , scan rate 0.1 V/s.

Palladium dissolves electrochemically in the carbamide and carbamide-chloride melts without passivation (Fig. 3). Its ions can be reduced at the electrode to the metal both in pure and  $K_2PdCl_4$ -containing melts. In all cases, the rate of electroreduction is very high, and the metal is deposited as a fine-crystalline powder. Like platinum, palladium forms ammonia and ammonia-chloride complexes when being dissolved electrochemically in carbamide-containing melts.

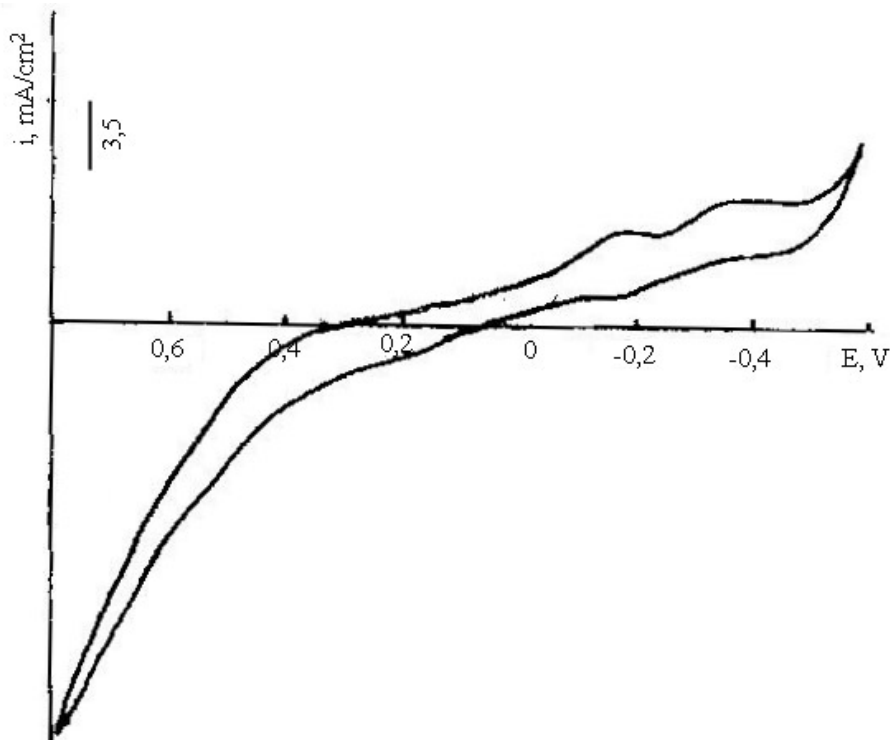


Figure 2. Cyclic voltammogram of a Pt electrode in the carbamide- $NH_4Cl$   $K_2PtCl_6$ -containing melt,  $t=130$  °C, scan rate 0.1 V/s.

Other metals (*Ti*, *Nb*, *Ta* [21, 22], *W*) are passivated in the carbamide and carbamide- $NH_4Cl$  melts, but the degree of their passivation is different, which is associated with the chemical properties of the metal, thickness and composition of the passive film, as well as with the solubility of the compounds forming the passive film in the melt. It should be noted that the composition of the film does not remain constant but undergoes changes on electrode polarization (Auger spectroscopic method). The electrochemical dissolution of metals that form a passive film in the carbamide- $NH_4Cl$  melt proceeds by the solid-phase mechanism of refractory metal dissolution [26], but the main characteristics of their electrochemical behavior differ from each other due to different degree of passivation.

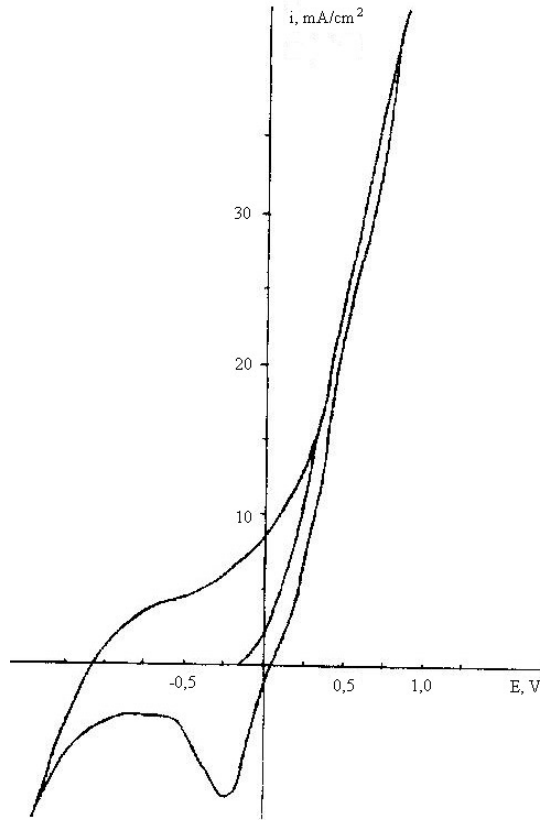


Figure 3. Cyclic voltammogram of a Pd electrode in the carbamide- $\text{NH}_4\text{Cl}$  melt,  $t=130^\circ\text{C}$ , scan rate 0.1 V/s.

Metals that are slightly passivated in the melt ( $W$ ,  $Ti$ ) should be classified as Group II. These metals are slightly but electrochemically soluble in pure carbamide. There is no dissolution wave at the forward anodic sweep, but at the backward sweep a small wave appears, which increases gradually from cycle to cycle (Fig. 4). By using gravimetry and UV/VIS spectroscopy it was shown that ions of the highest oxidation state ( $W(VI)$  and  $Ti(IV)$ ) in the form of isocyanate complexes of the respective metal are formed in the melt.

In the carbamide- $\text{NH}_4\text{Cl}$  melt, a  $W$  and  $Ti$  dissolution wave is observed during the very first cycle in the anodic part of the polarization curve (Fig. 5). The  $\text{Cl}^-$  ion, being a relatively weak depassivator, is able to dissolve the metals. Titanium is transferred into the melt as  $Ti(III)$  ions (Fig. 6, curve 1) and tungsten as  $W(V)$  ions. Further oxidation with the formation of ions in the highest oxidation state takes place upon approaching the solvent decomposition potential. The formation of  $W(VI)$  can be observed only by

UV/VIS, but the waves corresponding to the processes  $Ti(II) \rightarrow Ti(III)$  and  $Ti(III) \rightarrow Ti(IV)$  appear in reverse anodic curve after cycling to transpassive region (Fig. 6, curve 2). These waves are present in the subsequent forward sweep [22]. According to UV/VIS spectroscopy,  $Ti(II)$  octahedral complexes, type  $[Ti(KA)_6]^{2+}$ , and  $Ti(III)$  tetrahedral complexes, type  $[Ti(KA)_4]^{3+}$ , are formed during electrolysis at 5-20 mA/cm<sup>2</sup> and 30-50 mA/cm<sup>2</sup>, respectively. We failed to detect the formation of  $Ti(IV)$  ions due to the possible overlapping of charge transfer of  $Ti(IV)$  complexes by d-d transition of  $Ti(II)$  and  $Ti(III)$  complexes.

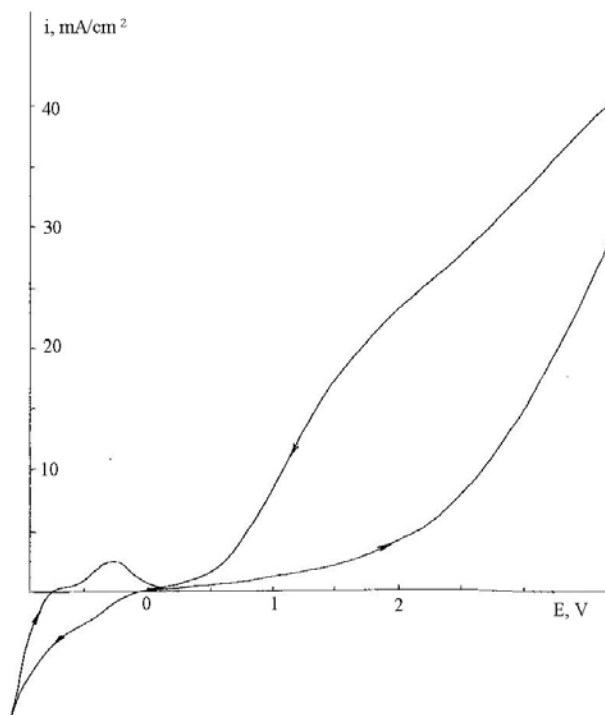


Figure 4. Cyclic voltammogram of a Ti electrode in the carbamide melt,  $t=130\text{ }^{\circ}\text{C}$ , scan rate 0.1 V/s.

Cathodic curves reflect ions stepwise reduction to metal via the formation of intermediates  $W(III)$  and  $Ti(II)$ .

Upon electrochemical dissolution,  $Ti$  and  $W$  form in the melt carbamide ( $[Ti(KA)_6]^{2+}$ ,  $[Ti(KA)_4]^{3+}$ ) or carbamide-chloride ( $[W(KA)_2Cl_4]^{+}$ ) complexes of different structure.

**Group III** comprises metals with a strong passive film ( $Nb$ ,  $Ta$ ). They are totally passivated in the carbamide melt. Their passivation in the carbamide-chloride melt is also rather strong and the depassivating action of  $Cl^-$  ions is insufficient to dissolve these

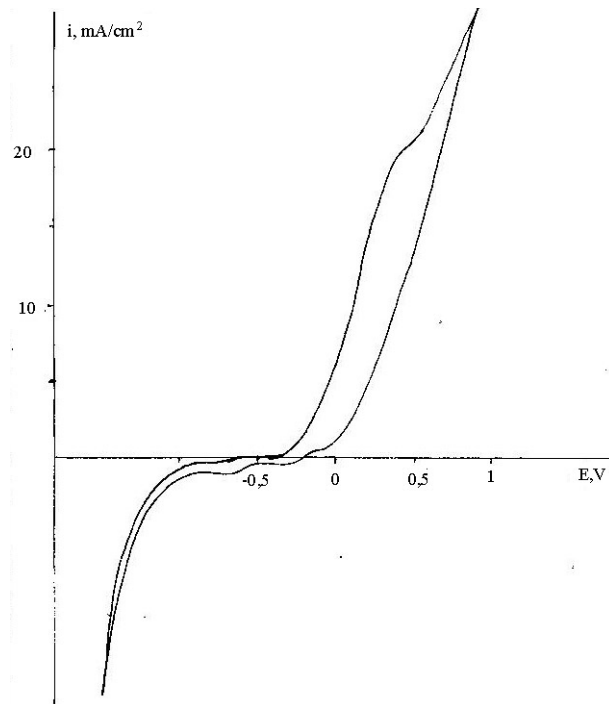


Figure 5. Cyclic voltammogram of a W electrode in the carbamide-NH<sub>4</sub>Cl melt,  $t=130^{\circ}\text{C}$ , scan rate 0.1 V/s.

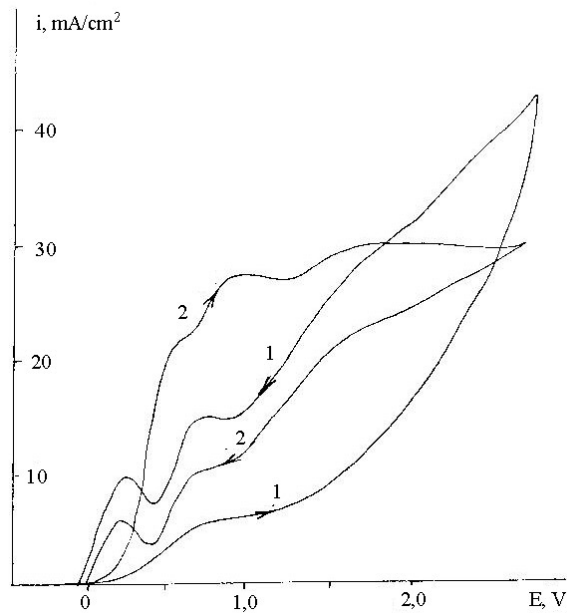


Figure 6. The anodic part of the cyclic voltammogram taken at a Ti electrode in the carbamide-NH<sub>4</sub>Cl melt,  $t=130^{\circ}\text{C}$ , scan rate 0.1 V/s.

metals [21, 23]. The electrochemical behavior of *Nb* and *Ta* in the carbamide- $\text{NH}_4\text{Cl}$  melt has some features. There is no *Nb* dissolution during the first polarization (Fig. 7, curve 1). As it was shown by us earlier [24], only after reaching the transpassive potential region, where a reactive compound (presumably  $\text{NCl}_3$ ) is formed which is the electrode surface depassivator, *Nb* dissolution wave appears at the backward sweep. *Nb* dissolution may be observed at the forward sweep in subsequent cycles (Fig. 7, curves 2-4). The cathodic reduction of *Nb(V)* ions formed in the melt upon the electrochemical dissolution of the metal takes place only at a *Nb* electrode (in contrast to inert *Pt* and glassy carbon electrodes) after electrode pre-polarization to the anodic region. The cathodic wave corresponds to the recharge of *Nb(V)* – *Nb(IV)* ions. We failed to detect the formation of ions in the lowest oxidation state (by electrochemical and spectroscopic methods). *Nb(V)* and *Nb(IV)* ions are in the melt in the form of chloride complexes, such as  $[\text{NbCl}_6]^-$  and  $[\text{NbCl}_6]^{2-}$ .

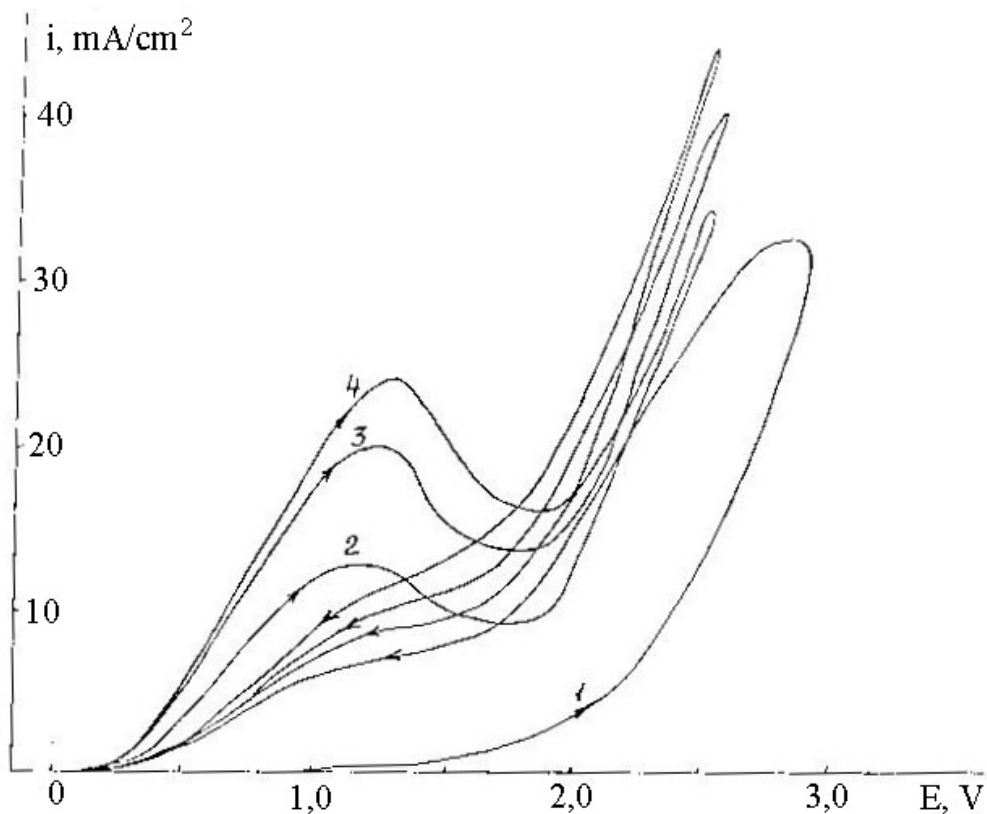


Figure 7. The anodic part of the cyclic voltammogram taken at a *Nb* electrode in the carbamide- $\text{NH}_4\text{Cl}$  melt,  $t=130^\circ\text{C}$ , scan rate 0.1 V/s.



The passivation of a *Ta* electrode is more pronounced than that of a *Nb* electrode. One pass to the transpassive region is insufficient for the *Ta* dissolution wave to appear in the cyclic voltammogram, i.e. the amount of depassivator that is formed within one cycle at potentials  $>0.1$  V is insufficient to depassivate the *Ta* surface. To accumulate the depassivator, either repeated cycling or decreasing the polarization rate or pre-electrolysis at transpassive region potentials is needed. In these cases, the metal dissolution wave can be observed, which corresponds to the formation of ions in the highest oxidation state (gravimetry, spectroscopy). However, the electrochemical reduction of *Ta(V)* takes place neither in the bulk of the melt nor on the electrode surface (*Ta*, *Pt*, glassy carbon). During the electrochemical dissolution of tantalum in the carbamide- $NH_4Cl$  melt, chloride complexes  $[TaCl_6]^-$  are formed.

#### 4. Discussion

Comparing the results of the investigation of the mechanism of electrode processes and the state of refractory metal ions formed upon electrochemical dissolution in the carbamide- $NH_4Cl$  melt, we can point out the following:

During the electrochemical dissolution of metals that are not passivated (*Pt*, *Pd*) in the carbamide- $NH_4Cl$  melt (in the presence of complex chlorides of these metals), ammonia chloride complexes are formed and then they are discharged at the cathode to deposit pure metals [27].

In the case of weak passivation (*W*, *Ti*), the electrochemical dissolution of metals involves the formation of their carbamide (chloride) complexes in the medium and highest oxidation state, the reduction of these complexes to metal proceeds stepwise via the formation of intermediates. The cathodic deposit consists mainly of oxy-chloride compounds of metals in the lowest oxidation state, while the quantity of pure metals is negligible.

The electrochemical dissolution of metals that are characterized by strong passivation (*Nb*, *Ta*) involves the formation of chloride complexes of ions in the highest oxidation state, whose reduction either does not take place at all (*Ta(V)*) or the recharge of metal ions  $Nb(V) \rightarrow Nb(IV)$  takes place to form a compound in lower oxidation state, which is soluble in the melt. Therefore, the formation of any cathodic deposit is ruled out in this particular case.

The passivation ability of *Ti*, *Nb*, *Ta* in the carbamide- $NH_4Cl$  melt was used to develop the electropolishing of these metals [28-30].

#### 5. Conclusions

Based on the experimental results obtained and established the correlation between passivation effects and the electrochemical properties of metals it is possible to make conclusions about possibilities to use the carbamide-ammonia chloride melt both for

electroplating and electropolishing. The melt can be used to obtain pure metals in the form of powders or electrodeposits if the metal is not passivated, and for the electrochemical treatment and surface polishing in the case of metal surface passivation.

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