The Polysurface Mechanism of Ta and Ti Anodic Dissolution in Low-Temperature Carbamide-NH_4CL Melt

S. Volkov, N. Tumanova, S. Kothetova, and N. Buryak

Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Kiev,
Pr. Palladina 32/34

Reprint requests to Dr. N. T.; Fax: +(38044) 444-30-70; E-mail: tumanova@ionc.kar.net

Z. Naturforsch. **56 a,** 761–763 (2001); received August 8, 2001

Presented at the NATO Advanced Study Institute, Kas, Turkey, May 4 - 14, 2001.

In this work the peculiarities of the electrochemical dissolution of tantalum and titanium in carbamide containing low temperature melts were studied.

Key words: Carbamide; Tantalum; Titanium; Electrochemistry; Passivation.

1. Introduction

The investigation of electrode processes with participation of refractory metals (Ta, Ti) in different high-temperature melts was conducted by a large number of authors for several decades. The interpretation of the experimental results is ambiguous because of polyvalent changes that take place at the electrodes. In one of the latest reviews [1], a systematization of the findings was performed. We failed to find literature data on electrode processes on refractory metals in low-temperature melts, except our investigations [2, 3].

The aim of this work is to study the peculiarities of the electrochemical dissolution of tantalum and titanium in carbamide containing low temperature melts.

The electrochemical study of the anodic behaviour of metals in a carbamide-ammonium chloride (16.8 mol.%) melt was conducted by recording cyclic voltamperic curves with a PI-50-1 potentiostat. A metal electrode with a working surface of $5.8 \cdot 10^{-3}$ m^2 was used as a working electrode. The auxiliary electrode was platinum plate. The potential was measured against a silver reference electrode (Ag/carbamide + NH_4NO_3 (16 mol.%) + 0.07 mol kg^{-1} $AgNO_3$). Experiments were carried out in the temperature range 100 to 140 °C under argon.

The state of the metal ions in the melts was investigated by spectroscopic methods: UV/VIS were taken during anodic (j_a = (5 - 150) mA/sm^{-2}) dissolution of metals with Specord UV/VIS and IKS-14 spectrophotometers, and Raman spectra, taken in 'quanced' melts (DFS-24 spectrometers). The electrode surface was analyzed in with Auger-spectrometer 09 IOS-1. The reagents (carbamide and salts) were dried in argon, and their mixtures were predried in vacuum at 80 °C.

During the investigation of Ta- and Ti-electrochemical dissolution it was found that these metals are passive in carbamide-based melts, but the degrees of their passivation are different. The composition of the passive film in the stationary state and under polarisation of the anode was studied by Auger spectroscopy. A carbamide film is generally formed on the metal (Ta, Ti) surface in the stationary state. During polarisation of the electrodes, the composition of the films changed.

In case of the Ta electrode, the concentration of oxygen increases and the surface film is converted into an oxide film. In case of Ti, the changes of the surface film during the first steps of polarisation are negligible, but gradually the oxygen and chlorine concentration increases and oxychloride of Ti is formed on the electrode surface at potentials > 0.25 V. Therefore the dissolution of these metals has peculiarities.

The depassivation of the carbamide film formed on the Ti electrode takes place comparatively read-

0932–0784 / 01 / 1100–0761 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

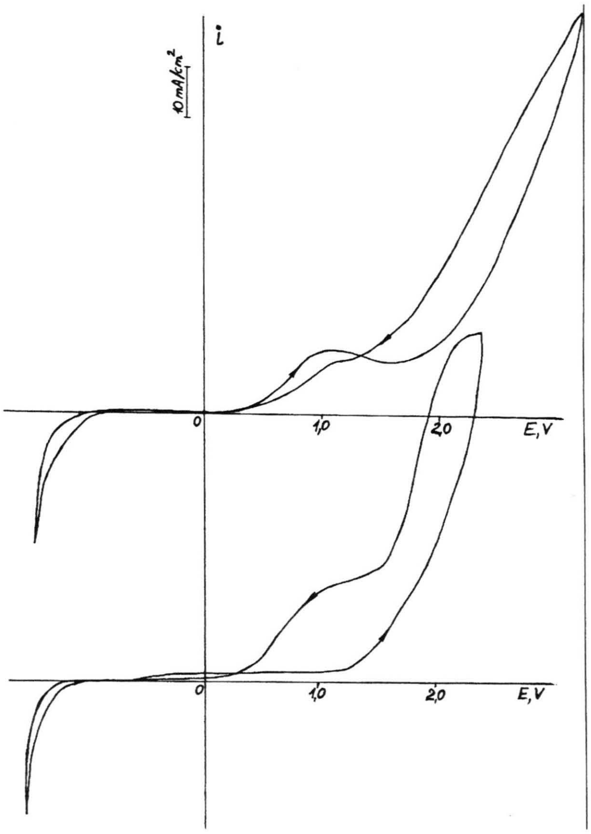

Fig. 1. Cyclic voltamperogramm of a Ti electrode in carbamide-NH_4Cl melt at 130 °C; scan rate: 0.1 V/s.

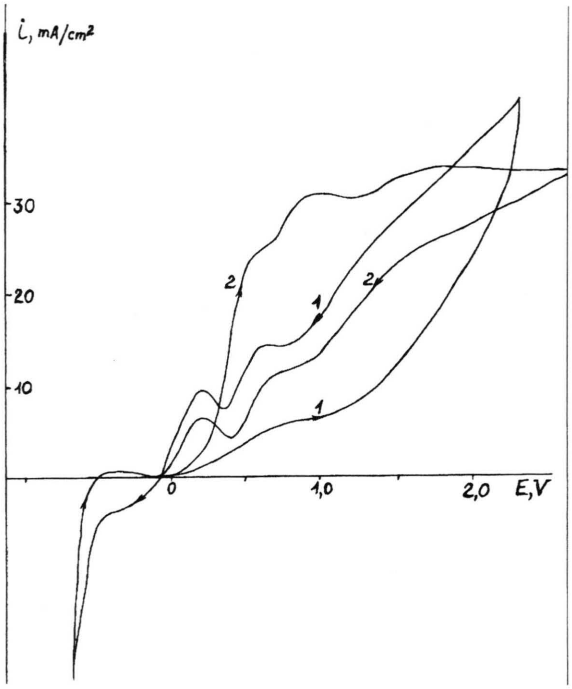

Fig. 2. Cyclic voltamperogramm of a Ta electrode in carbamide-NH_4Cl at 130 °C: the first cyclic curve and the cyclic curve after 5 subsequent cycles; scan rate: 0.1 V/s; T = 130 °C.

ily. The titanium dissolution wave appears in the first forward cycle of the cyclogram of the Ti electrode in the carbamide-NH_4Cl melt. It follows that the depassivation of Cl^- is sufficient for Ti electrodissolution and formation, according gravimetric and spectroscopic data, of octahedral complexes $[Ti(CO(NH_2)_2)_6]^{2+}$ in the melt. But the oxychloride formation on the Ti surface under polarisation leads to an increase of the electrodes passivation. As a result, in the first cycle only one wave is observed on the cyclograms. After increasing the positive potential and reaching the transpassive potential region, however, two more waves appear on the reverse sweep at more positive potentials than the Ti(II) wave. (It was shown by us [2] that, at a potential larger than 1 V, the depassivator (NCl_3) is formed during the electrolyse of the carbamide-NH_4Cl melt.) All three waves are observed in the subsequent cycles of anodic cyclic voltammograms. They reflect the sequential oxidation of Ti(II) to Ti(III) and Ti(IV) (gravimetric and spectroscopic data). It is meant, that for depassivation of a Ti oxychloride film, formed on the Ti electrode, a stronger depassivator (NCl_3) than for carbamide film depassivation (Cl^-) is necessary.

The main cause that determined the peculiarities of the electrochemical behaviour of tantalum in a carbamide-chloride melt is the strong passivation of the metal. Due to formation of an oxide film on the Ta surface, under polarisation the metal dissolution wave is absent in the two or three subsequent cycles when taking the anodic part of cyclograms, cf. Figure 2. When taking a full cyclic voltammogram, the tantalum dissolution wave appears only in the fifth or sixth cycle due to the growth of a passive film while the electrode stays in the melt. For the appearance of the dissolution wave, the formation and accumulation of a certain amount of depassivator in the transpassive region on repeated cycles is necessary. To accumulate the depassivator, repeated cycling is not necessary. The electrolysis can be carried out in 15 and more minutes at the potentials of the transpassive region; then the tantalum dissolution wave can be observed right away in the first cycle. After electrochemical dissolution, Ta is transferred into the melt as octahedral complexes, type $[TaCl_6]^-$.

The peculiarities of the Ti and Ta electrochemical dissolution in carbamide-NH_4Cl may be caused by a different degree of passivation, different composition of the passive film and different solubility of metal compounds that form the passive films.

[1] A. Girginov, T. Tzvetkoff, and M. Bojinov, J. Appl. Electr. 25, 993 (1995).
[2] S. Volkov, N. Tumanova, E. Babenkov, V. Bandur, and N. Burjak, J. Electroanalytical Chem. Soc. **424**, 13 (1997).
[3] N. Tumanova, E. Babenkov, V. Bandur, and V. Trachevsky, Ukr. Chim. J. **66**, 35 (2000) (In Russian).