

KINETICS AND MECHANISM OF ELECTROLYTICAL
CORROSION OF TITANIUM BASED CERAMICS IN 3% NaCl
SOLUTION

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Several literature data are concerned with high-temperature oxidation of multiphase non-oxide ceramic systems, such as TiB_2 -AlN, AlN-SiC, Si_3N_4 -TiN,.... Conversely, there are only rare information about corrosion resistance of these electroconductive ceramic composites by sodium chloride solution although they can find various applications including their use in marine water.

Therefore, the electrolytic corrosion of hot isostatically pressed titanium nitride-aluminum nitride (TiN-AlN), titanium diboride-aluminum nitride (TiB_2 -AlN), titanium diboride-titanium nitride (TiB_2 -TiN) composites or monolithic titanium diboride TiB_2 and titanium carbonitride $TiC_{0.5}N_{0.5}$ ceramics was studied at 20°C in a 3% sodium chloride (NaCl) solution. The electrolyte used in this study imitates, by its composition, the marine water.

The kinetics were recorded by using a potential-dynamic method which gives polarization curves (Fig. 1-3). For the determination of the oxidation mechanism, the chemical analysis of the solution (titanium ions state) as well as XRD, SEM and AES analysis of the oxidized sample surface layers were used.

In all cases, the oxidation of the above ceramics proved to be a multistep process, the peculiarities of the different steps were discussed on the basis of experimental data obtained by the pointed out methods. After an initial anodic dissolution, with transfer of Ti^{3+} , TiO^{2+} ions or/and H_3BO_3 into the solution, the formation of TiN_xO_y , $TiC_xN_yO_z$ or TiO_2 (rutile) partially protecting layers takes place, the latter oxide slows down the dissolution of the composites.

At low anodic potentials, the oxidation resistance only slightly decreases in the sequence: (TiN-AlN) \rightarrow (TiB_2 -AlN) \rightarrow (TiB_2 -TiN) \rightarrow $TiC_{0.5}N_{0.5}$. At high anodic potentials, the TiN-AlN and TiB_2 -AlN ceramic composites behave in a similar way. The outer protective layer which is formed on the surface, proved to be a mixture of γ -Al(OH)₃ and AlO(OH) phases. On the surface of oxidized TiB_2 -TiN ceramics (at potentials greater than + 2.0 V), an extremely thin titanate layer containing both Na_4TiO_4 and Mg_2TiO_4 was detected by AES. Concerning the carbonitride $TiC_{0.5}N_{0.5}$, at anodic potentials up to + 1.8 V, a rutile TiO_2 film is found on the surface which presents less protective properties.

In conclusion, it is shown that the corrosion resistance of the above binary ceramics in a 3% NaCl solution is exceptionally high. The electrolytic corrosion rate of composites is proved to be approximately by three orders lower than the dissolution rate of a dense titanium diboride material. Therefore, we can recommend the use of these ceramics in marine water and anticipate their development as high-performance materials in such corrosive environment.

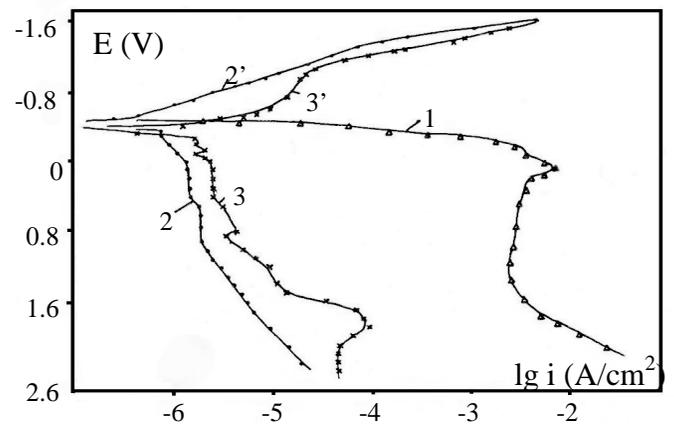


Fig. 1. Anodic polarization curves for : 1- TiB_2 , 2- TiB_2 -AlN sample after polishing, 3- TiB_2 -AlN sample after hydrogen treatment, 2'-cathodic curves straight run, 3'-reciprocal run

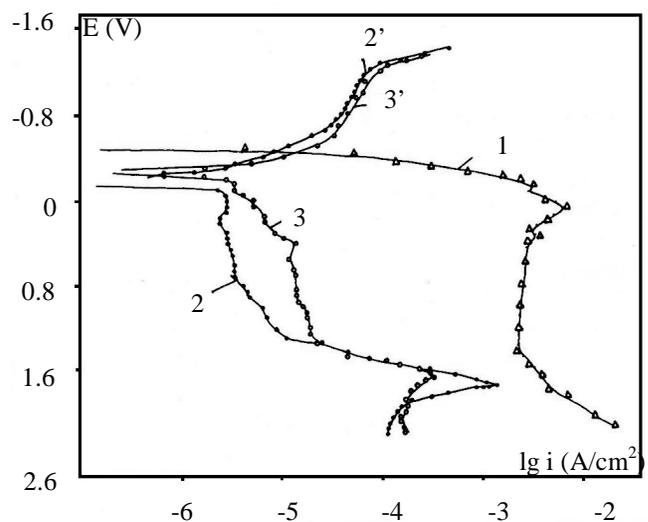


Fig. 2. Anodic polarization curves for : 1- TiB_2 , 2- TiB_2 -TiN sample after polishing, 3- TiB_2 -TiN sample after hydrogen treatment, 2'-cathodic curves straight run, 3'-reciprocal run

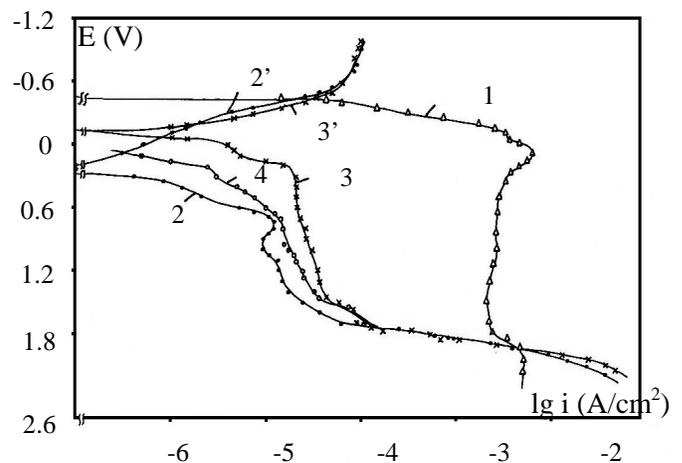


Fig 3. Anodic polarization curves for : 1- TiB_2 , 2- $TiC_{0.5}N_{0.5}$ sample without treatment, 3- $TiC_{0.5}N_{0.5}$ sample after hydrogen treatment, 4.-after polishing, 2'- $TiC_{0.5}N_{0.5}$ cathodic curves straight run, 3'-reciprocal run