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Influence of material structure on the electrochemical behavior of nickel–titanium carbonitride composites

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ABSTRACT

Ni–$TiC_{0.7}N_{0.3}$ composites were prepared using direct current electrodeposition and hot pressing routes. Hot pressed Ni and sintered $TiC_{0.7}N_{0.3}$ were also prepared. In case of electrodeposition, the samples contained between 10.4vol.% and 20.9vol.% $TiC_{0.7}N_{0.3}$. The hot pressed composite contained 16.7vol.% $TiC_{0.7}N_{0.3}$. The Ni based materials exhibited active–passive behavior in de-aerated 0.1mol/l H_2SO_4 solution, while $TiC_{0.7}N_{0.3}$ exhibited active behavior. The corrosion rate and passive current density increased and critical current density decreased with increase in reinforcement volume fraction. Based on microscopic examination, the increase in passive current density has been related to the increase in matrix area due to selective corrosion at metal–ceramic interfaces.

1. Introduction

Titanium carbonitride based cermets have received great attention as cutting tool inserts due to high hardness, enhanced wear resistance and chemical stability at elevated temperatures [1–7]. In order to control toughness, nickel, cobalt and/or iron powder is usually added as binder [3–11]. Thus, cermets are heterogeneous materials and therefore undergoes galvanic corrosion in acidic environments as the ceramic phase is usually noble with respect to the binder phase [12–19].

Some results pertaining to electrochemical studies of cermets are as follows. In alkaline and neutral environment, cermets are generally corrosion resistant at room temperature [20]. Attack by chlorides is more severe compared to sulfates [17]. Role of oxygen in enhancing corrosion rate has been found to be insignificant in aerated environment [17]. However, usually de-aerated solutions are used for electrochemical tests. Stern linear rule of mixture [21] to relate corrosion rate with respect to ceramic and binder area ratio has been found valid for cermets [15].

Limited literature is available on electrochemical properties of titanium carbonitride based cermets. Lavrenko et al. [7] prepared $TiC_{0.5}N_{0.5}$ ceramic using hot isostatic pressing without any additive. They then performed potentiodynamic polarization in 3% NaCl electrolyte at 20°C. After polarization, they characterized oxidized surface through chemical analysis, scanning electron microscopy, X-ray diffraction and Auger electron spectroscopy. They concluded that oxidation of the ceramic is a multistage process. They further concluded that the ceramic has exceptionally high corrosion resistance as there was no binder phase. In another study by Kumar et al. [22], $TiC_{0.7}N_{0.3}$-20wt.% Ni cermet was studied by potentiodynamic polarization in 0.2mol/l sulfuric acid. They noticed two passive regions in the potentiodynamic curve. They attributed

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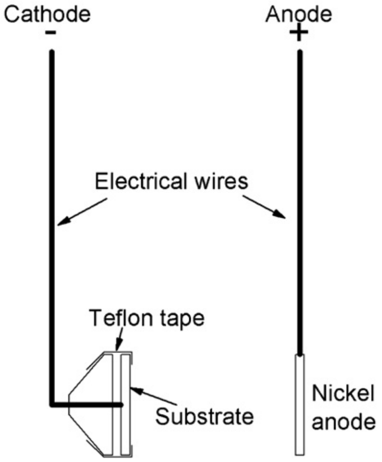

Fig. 1 – Schematic of experimental cell assembly utilized for electrodeposition.

passive region at lower potential due to passivation of $TiC_{0.7}N_{0.3}$ while the passive region at higher potential due to passivation of nickel.

Two major causes of corrosion have been noticed in cermets with multiple phases. One is galvanic corrosion due to significant difference in corrosion potentials of different phases and other is crevice corrosion in pores. Since the ceramic phase (nobler phase) is usually the major phase in cermets, the cathode to anode area ratio might play an important role. Cermets unavoidably contain pores as they are processed through sintering or hot isostatic pressing. In various systems, presence or formation of pores has been found detrimental to corrosion properties. Some examples showing decrease in corrosion resistance due to porosity are discussed as follows.

Jegannathan et al. [23] found poor corrosion resistance of phosphate coatings obtained by anodic treatment. They attributed this to the creation of pores during anodic treatment. Gu et al. [24] found high corrosion resistance of nanocrystalline nickel coating on AZ91D magnesium alloy due to low porosity and fine grain structure. Liu et al. [25] studied corrosion and wear performance of HVOF-sprayed Inconel 625 and WC-Inconel 625 coatings treated with high power diode laser. They achieved significant improvement of corrosion and wear resistance after laser treatment as a result of the elimination of discrete splat-structure, micro-crevice and porosity, and also the reduction of microgalvanic driving force between the WC and the metal matrix. Herrasti et al. [26] obtained polypyrrole coating by applying a constant current on copper with high corrosion resistance due to lower porosity. Chandramouli et al. [27] performed corrosion studies of sintered powder metallurgy plain carbon steel preforms. They attributed enhanced rate of uniform corrosion in both Fe and Fe-1%C carbon steels due to presence of porosity. Ahn et al. [28] studied corrosion behavior of TiN hard coatings produced by a modified two-grid attachment magnetron sputtering process. They found accelerated localized corrosion due to presence of pores.

Factors like crevice corrosion due to presence of pores and galvanic corrosion due to different phases (ceramic and binder phase) determine the electrochemical properties of cermets. It is therefore important to understand the independent effect of porosity and the binder phase on corrosion. The present study was undertaken to understand the effect of material structure on the electrochemical behavior of titanium carbonitride in a fully dense binder phase. This was achieved by co-deposition of titanium carbonitride in nickel matrix. To study the effect of porosity in the binder phase, hot pressed nickel sample was prepared. To test the combined effect of both porosity and titanium carbonitride particles, hot pressed nickel titanium carbonitride composite was also prepared. The secondary aim of the present study was to compare the electrochemical behavior of Ni-based materials with that of bulk nickel.

2. Experimental

Ni–$TiC_{0.7}N_{0.3}$ electrodeposited samples were prepared using 150ml Watt's bath (of composition $NiSO_4 \cdot 6H_2O$ 250g/l, $NiCl_2 \cdot 6H_2O$ 30g/l, H_3BO_3 40g/l). NaOH was added to the Watts bath to adjust pH to 4. A 2g/l suspension of $TiC_{0.7}N_{0.3}$ particles (H. C. Starck, USA) of size 3 to 4μm was used in all experiments. Copper substrate of area 3cm × 3cm, polished up to 1000 grade SiC paper, served as the cathode. Before each eletrodeposition experiment, the substrate was ultrasonically cleaned and degreased using acetone. The cathode was electrically insulated at the back face and edges (using perspex sheet and teflon tape) and electrical connection was provided at the back, as shown in Fig. 1. Nickel anode was placed 5cm away from the cathode. The deposition direct current density and bath temperature used are mentioned in Table 1. The time of electrodeposition was adjusted such that a charge of 540 C/cm^2 was used for every electrodeposition. Current efficiency was calculated from the known increase in weight of the sample after electrodeposition and the amount of $TiC_{0.7}N_{0.3}$ codeposited.

Hot pressed Ni-16.7vol.% $TiC_{0.7}N_{0.3}$ composite and pure Ni were prepared using Ni powder (of size 20μm) in a graphite mould, which was maintained at a high temperature by resistance heating. The composition of the composite (i.e., 16.7vol.% $TiC_{0.7}N_{0.3}$ equivalent to 10wt.% $TiC_{0.7}N_{0.3}$) was chosen such that it is close to the average amount of $TiC_{0.7}N_{0.3}$ reinforced in electrodeposited samples, for comparison of properties. A hydraulic pressure of 1.5MPa was maintained during hot pressing. Hot pressing was conducted in open atmosphere. $TiC_{0.7}N_{0.3}$ sintered sample was prepared by first cold compacting the powder at 102MPa and then sintering in vacuum at 1950°C

Table 1 – Sample preparation and characteristic physical parameters of electrodeposited composites

Sample no.	1	2	3	4	5	6	7	8	9
Current density (mA/cm^2)	25	50	100	25	50	100	25	50	100
Temperature (°C)	30	30	30	40	40	40	50	50	50
Current efficiency (%)	90.9	93.8	92.6	94.1	88.8	87.2	94.6	92.2	88.7
$TiC_{0.7}N_{0.3}$ (vol.%)	12.3	10.7	15.5	15.0	20.9	18.1	10.4	11.8	14.7