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Galvanic corrosion of metal/ceramic coupling

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ABSTRACT

The galvanic corrosion risk of metal/SiC-based ceramic coupling in 3.5 wt% NaCl aqueous solution is investigated. Electrochemical measurements as linear sweep voltammetry and galvanic corrosion tests according to DIN-50919 were used. The results clearly show that the resistivity of the SiC-based ceramic plays the key role in the understanding of galvanic corrosion between metal and ceramic. In all cases the ceramic represents the cathodic site of the coupling. The corrosion rate is dominated by the electrical resistance of the ceramic.

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1. Introduction

Modern engineering structures are frequently created as mixed material constructions with various couplings of materials. Couplings of two or more dissimilar metals or metals with electron conductive non-metals are highly susceptible to corrosion under the following conditions [1–3]:

- (i) The materials are in electrical contact.
- (ii) The materials are exposed in the same electrolyte.
- (iii) A potential difference (usually >50 mV [3]) has to exist between the different materials.

Under these conditions the material coupling represents a galvanic cell where the material with the more negative electrode potential forms the anode and its corrosion can be severely accelerated. This so called galvanic corrosion is well known and reported in an abundance of papers over many decades (see e.g. [4– 19]). A brief but impressive introduction into the theory of galvanic corrosion and the most important influencing variables is given by Oldfield [33]. The examples of galvanic corrosion are very widespread from orthopedic implants [13] and welds [19] to automotive manufacturing [12,14], aircraft construction [11] and shipbuilding [10]. Extended investigations and theoretic treatments of galvanic corrosion between couplings of dissimilar structural materials are reported by Mansfeld and co-workers [34–37]. However, the same corrosion mechanism takes place on microscale in the case of heterogeneous microstructures of materials, e.g., age-hardenable aluminum alloys [20,21], duplex steels [22] and cermets [23,24] also designated as "internal bimetallic corrosion" [23]. Sometimes cermets are used as protective coatings to enhance hardness and wear resistance [25]. Thereby, a galvanic coupling between the ceramic coatings and the substrate material (e.g., steel) can be created, depending on the defects of the coatings (e.g., pores, cracks). The special case of metal ceramic couples on the microscopic scale, so-called metal matrix composites (MMC). is relatively intensively investigated (see e.g. [26,27]). In contrast to this, the corrosion behavior of the macroscopic material compound consisting of a metal ceramic coupling is de facto next to nothing reported in the electrochemical focused literature. In the late 1950, Podbreznik [28] tried to define the term "contact corrosion" generally as corrosion of a material in contact with another and distinguished between the corrosion of metal/metal contacts, the corrosion between non-metallic materials and the corrosion of a metal/non-metal coupling. This classification he reported on the corrosion of aluminum in contact with concrete and mortar. However, nowadays the term "galvanic corrosion" is usually used as corrosion between dissimilar metals which are in electrical contact. By definition "galvanic corrosion" is the corrosion between various electronic conductive or semi-conductive materials which are in contact and exposed in the same electrolyte.

In this work the authors just present the results of the electrochemical investigation of a metal/ceramic coupling. The ceramic is a semi-conductive SiC-based material. Therefore, the term galvanic corrosion is correctly used in view of the aforementioned definition.

Owing to their extended behaviors in view of tribology, wear and corrosion protection, SiC-based materials are in widespread use under high chemical and abrasive stress, e.g., in bearings, sealings in chemical industrial facilities, automotive industry and power plant engineering.





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2. Materials and methods

2.1. Materials

The material couple consists of a metallic part and a ceramic part. The metallic parts were used in both cases and were pure nickel (99.99 wt%; Chempur) as well as unalloyed steel DC01 (0.12 wt% C; Georg Martin GmbH) with hypoeuthectoide microstructure. Two different SiC-based ceramics were used in the present work. One of them, EKasic®D (ESK Ceramics GmbH) later termed SiC I, is a solid phase sintered silicon carbide (SSiC) containing a small amount of aluminum (0.5 wt%) as a sintering additive. The incorporation of aluminum into the silicon carbide grains results in a high doping level and increases the electric conductivity. The microstructure of SiC I is dominated by a relatively fine grained SiC-phase (Fig. 1). Additionally, a small amount of residual carbon and very few small pores are visible in the micrograph.

The other one was the material SiC30 (Schunk Kohlenstofftechnik), later termed as SiC II. SiC30 is declared as a SiC-graphite composite material (\approx 35 wt% C, \approx 3.0 wt% free Si) [38]. The microstructure of SiC II consists of large areas of un-reacted carbon surrounded by a three-dimensional network of SiC and free silicon (Fig. 2). The material is produced by the reactive Si infiltration of carbon. Resistivities of the materials are shown in Table 1.

Before electrochemical experiments the metal samples were only cleaned in ethanol and rinsed with deionized water. The surface area amounts to 10 cm².

The SiC-based materials were electrically contacted and embedded in epoxy resin. The free surface was 1 cm². All ceramic samples were mechanically ground, polished with a diamond suspension up to 1 µm diamond grain size and rinsed with deionized water prior to the electrochemical investigation.

2.2. Methods

The electrochemical experiments on the individual materials were carried out in a conventional 3-electrode design using a flat cell. A computer controlled potentiostate Autolab 30 (Metrohm) was used for the linear sweep voltammetry (LSV) as well as the galvanic corrosion measurements. As a reference, electrode works on a saturated calomel electrode (Sensortechnik Meinsberg). A platinum sheet was used as counter electrode. All measurements were carried out in aerated sodium chloride solution (3.5 wt%, pH 6.5).

The galvanic corrosion experiments were carried out following DIN-norm 50919 [29]. The norm requires a measuring arrangement as schematically shown in Fig. 3. The distance between both

Fig. 1. FESEM micrograph of SiC I revealing the relatively fine grained structure (various gray areas) and some C-inclusions and pores (dark area).

Fig. 2. FESEM micrograph of SiC II showing the SiC (gray area), residual graphite (dark area) and residual Si (white area).

Table 1

Resistivity of the used material. The data of the metals originated from [32].

Material	SiC I	SiC II	Ni	DC01 ^a
Resistivity (Ω cm)	250	0.01	7×10^{-6}	1×10^{-5}

^a The resistivity of DC01 is assumed to iron.



Fig. 3. Schematic drawing of the experimental setup investigating galvanic corrosion following the DIN-norm 50919 [29].

electrodes amounts to 3 cm. The relation of the surface between the ceramic samples and the metallic materials amounts to 1:10. This relation considers that in technical constructions the ceramic is often embedded in a distinctly larger metallic design.

3. Results and discussion

Fig. 4 shows the open circuit potentials (OCPs) of nickel and steel (Fig. 4a) as well as the SiC-based ceramics (Fig. 4b). The OCP is stable after only few minutes. In the case of the pretreated SiC-based ceramic the OCP is identical to the unpretreated ceramic state after 30 min. This is caused by the formation of the oxide film which was removed by the pretreatment in hydrofluoric acid. According to the discussion in Section 1 the potential difference ΔE between the material SiC I–Ni ($\Delta E \approx 165$ mV), SiC I–DC01 $(\Delta E \approx 475 \text{ mV})$ and SiC II–DC01 $(\Delta E \approx 400 \text{ mV})$ fulfills the thermodynamic precondition for galvanic corrosion. The potential difference between SiC II–Ni ($\Delta E \approx 90 \text{ mV}$) is close to the criteria discussed in Section 1. With respect to the usual variation of the potential of technical materials it seems possible that the potential differences can be too small in a given case.





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