Corrosion study of electroplated nickel metal-matrix composites with B_4C, Al_2O_3 and SiC

Mykolas Gladkovas,
Viktorija Medelienė,
Meilutė Samulevičienė and
Eimutis Juzeliūnas[*]

Institute of Chemistry,
A. Goštauto 9,
LT-2600 Vilnius, Lithuania

Corrosion of nickel metal-matrix composites (Ni-MMC) containing B_4C, Al_2O_3 and SiC particles has been studied by an accelerated corrosion test in neutral and acid salt fog. The electrochemical behavior of the MMC has been investigated in neutral and acid solutions by means of voltammetry and impedance spectroscopy. An accelerating effect of B_4C has been observed in both neutral and acid environments. Al_2O_3 inhibited corrosion in the acid environment and did not affect it in the neutral one. It has been concluded from voltammetric measurements that an increased corrosion susceptibility of Ni–B_4C composites was due to the acceleration of the partial anodic reaction, which is more favored on the metal–particle interface than on the rest of the surface. The impedance spectroscopy measurements did not reveal any significant differences in the corrosion electrochemical mechanism of pure Ni and Ni-MMC.

Key words: nickel, metal-matrix composite, accelerated corrosion testing, salt fog, electrochemical impedance spectroscopy, potentiodynamic polarization

INTRODUCTION

Metal-matrix composites (MMC) have a number of advantages over conventional metals and alloys. Incorporation of ceramic particles into a metal matrix leads to a superior specific strength, improved wear and heat resistance, self-lubrication, etc. [1]. While physical-mechanical properties of MMC have been extensively studied [2], relatively little information is available about the MMC corrosion behavior.

Corrosion of aluminum matrix composites has been studied most extensively. Various surface treatments have been investigated, *viz*. polymer coating, anodizing and chemical passivation [3], anodic hard coating [4], sulfuric acid anodizing [5, 6]. In recent years, Mansfeld et al. studied the corrosion behavior of aluminum alloys reinforced with SiC and Al_2O_3 particles by means of electrochemical techniques and SEM [7, 8]. Different methods of corrosion protection were applied to MMC: surface modification in $Ce(CH_3COO)_3$ and Na_2MoO_4 solutions; sulfuric acid anodizing and sealing in hot water, cerium nitrate and dichromate solutions. The effectiveness of the protection means depended on the matrix alloy rather than on the reinforcement material.

Different results have been reported concerning the effect of incorporated particles on the metal matrix corrosion. Greene and Mansfeld observed that Al–SiC and Al–Al_2O_3 composites had similar corrosion and pitting potentials as the metal matrix, whereas the oxygen reduction rate increased with the reinforcement concentration [3]. The authors attributed the increased corrosion susceptibility of MMC to the activity of interfaces between the metal and the particle. Benea showed that ZrO_2 inhibited copper corrosion in both sulphate and chloride solutions [9]. The effect was attributed to the crystallographic properties of MMC. Yagodkina et al. observed either the accelerating or inhibiting effect of nickel corrosion depending on the diamond particle size [10]. The authors concluded that differences in the corrosion rate were due to a different crystallographic structure of the nickel matrix. Bapu reported that corrosion resistance of Ni–BN composites decreased with the BN content in the metal [11].

Thus, the information concerning the effect of ceramic particles on the corrosion rate of the metal matrix is not complete. This work was aimed at conducting corrosion studies of electrochemically plated nickel coatings co-deposited with B_4C, Al_2O_3 and SiC particles.

---

[*] Corresponding author: ejuzel@ktl.mii.lt

ISSN 0235–7216. Chemija (Vilnius). 2002. T. 13, Nr. 1

EXPERIMENTAL

Nickel coatings were electroplated on a platinum base (1 cm^2) in a glass frame from the following bath: 300 g/l $NiSO_4 \cdot 7H_2O$, 45 g/l $NiCl_2 \cdot 6H_2O$, 30 g/l H_3BO_3, pH 4. The composite coatings were deposited from the same bath with the following additive: α-Al_2O_3 (concentration 150 g/l, the average particle size 10 μm), SiC (150 g/l, 2 μm) and B_4C (40 g/l, 5 μm). The bath was agitated with a stream of compressed air. The cathodic current density was 5 A/dm^2, the solution temperature was 55 °C. The thickness of coatings was 30 μm. The deposits contained about 3.7 mass % Al_2O_3, 5.5 mass % SiC and 7.3 mass % B_4C. The amounts of the particles were determined by weighing their mass after dissolving nickel in hydrochloric acid (1:1), filtering off and calcinating the particles at 350 °C [12, 13].

The coatings for corrosion studies in salt fog were deposited using the above-described procedure on copper plates with dimensions 10 × 5 × 0.1 cm. The plates were treated with a CaO and MgO mixture (mass ratio 1:1) and activated in hydrochloric acid (1:4).

Salt fog was produced by spraying 5% NaCl solution (pH 6–7) or the solution acidified by acetic acid (pH 3.3) into a corrosion chamber. The temperature in the chamber was 35 ± 1 °C. Other conditions were as established by the international standard [14]. The corrosion rate was estimated from the difference in mass of a non-corroded sample and a corroded one. Prior to weighing, the corrosion products were dissolved in hydrochloric acid, then the samples were washed in deionised water and finally dried within 24 h in a desiccator containing $CaCl_2$ [15]. The corrosion rates presented in figures were average values of 5 samples.

Voltammetric as well impedance measurements were carried out in naturally aerated 5% NaCl solution and in the same solution acidified with H_2SO_4 (pH 3.1) or acetic acid (pH 3.3). Experiments were conducted at room temperature (20 ± 2 °C). The standard Ag/AgCl reference electrode was used, and all data were given with respect to that electrode. A platinum plate served as a counter electrode. Polarisation and impedance measurements were conducted by using an IM 6 apparatus by Zahner (Germany).

RESULTS AND DISCUSSION

Figures 1 and 2 show the results of corrosion investigations of Ni-MMC in neutral salt fog (Fig. 1) and in acid one (Fig. 2). The corrosion rates of Ni–Al_2O_3 and Ni–SiC in neutral fog did not differ significantly from the corrosion rate of pure nickel, whereas the composite with B_4C corroded considerably much faster than other specimens. The accelerating effect of B_4C was also observed in acid fog (Fig. 2). The Al_2O_3 particles, however, tended to inhibit the corrosion process in the acid environment. Figures 1 and 2 also clearly show that in the acid environment all specimens exhibited much higher corrosion rates than in the neutral environment.

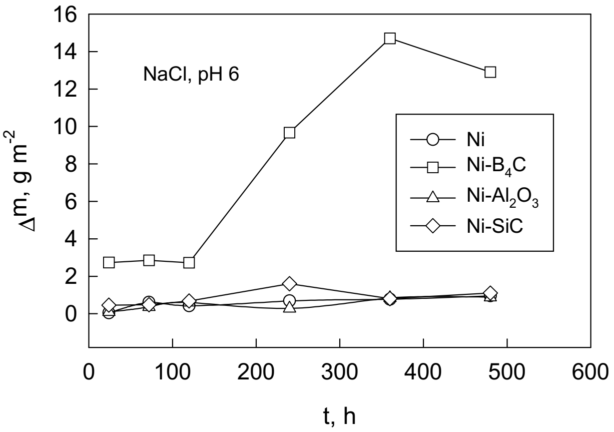

Fig. 1. Mass loss *vs*. time for Ni and Ni-MMC in neutral NaCl fog

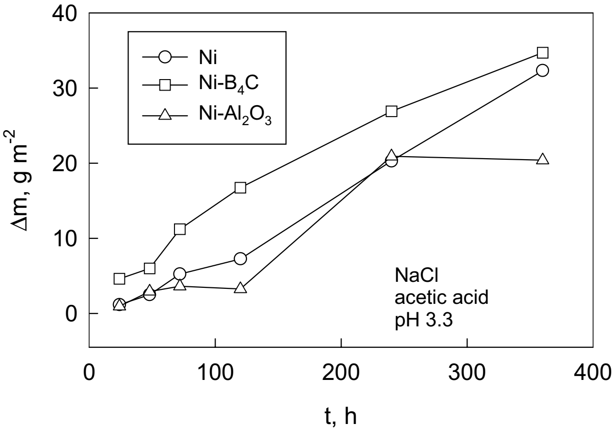

Fig. 2. Mass loss *vs*. time for Ni and Ni-MMC in NaCl + acetic acid fog (pH 3.3)

Figures 3–5 give results of Ni-MMC investigations by voltammetry in neutral 5% NaCl (pH 6, Fig. 3) and in a solution acidified by acetic acid (pH 3.5, Fig. 4) and sulphuric acid (pH 3.1, Fig. 5). One can see that in the neutral solution B_4C accelerates nickel anodic dissolution and inhibits the cathodic process, which should be ascribed mainly to the reaction of dissolved oxygen reduction. (To be precise, some contribution of Ni(II) reduction is also possible, because minor amounts of these ions are always present in the vicinity of the electrode). Acceleration of anodic dissolution by B_4C is also obvious in acid solutions (Figs. 4 and 5). The cathodic reaction, which is mainly caused by hydrogen

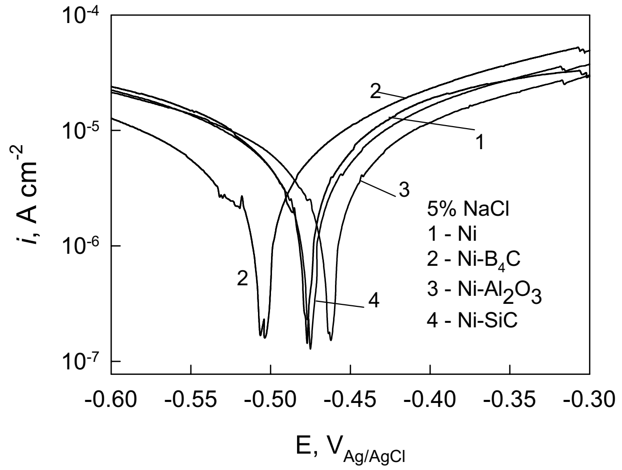

Fig. 3. Potentiodynamic curves obtained in 5% NaCl (pH 6) for Ni (1), Ni–B_4C (2), Ni–Al_2O_3 (3) and Ni–SiC (4). Potential scan rate 5 mV s^{-1}

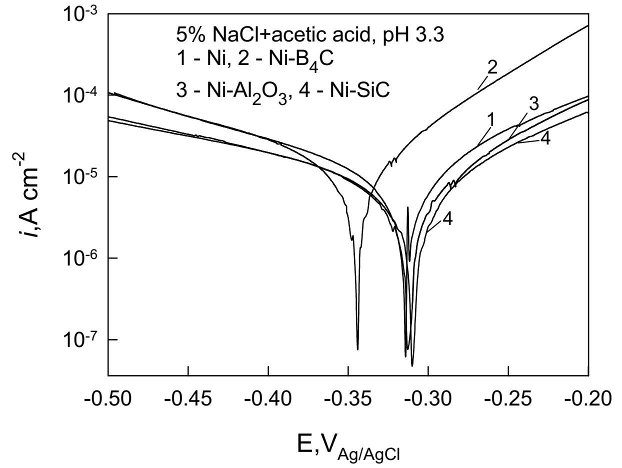

Fig. 4. Potentiodynamic curves obtained in 5% NaCl + acetic acid (pH 3.3) for Ni (1), Ni–B_4C (2), Ni–Al_2O_3 (3) and Ni–SiC (4). Potential scan rate 5 mV s^{-1}

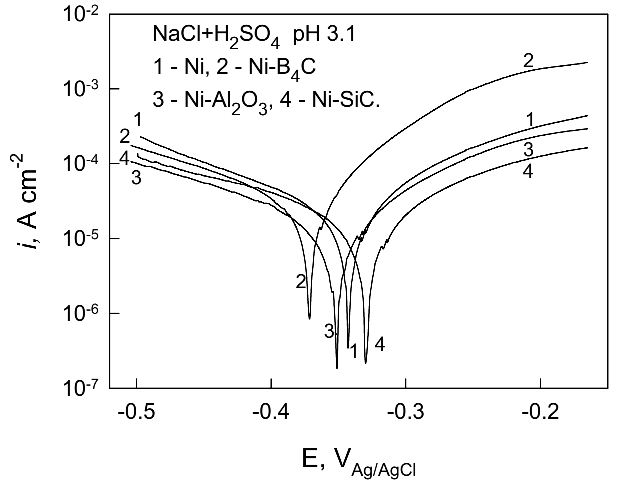

Fig. 5. Potentiodynamic curves obtained in 5% NaCl + H_2SO_4 (pH 3.1) for Ni (1), Ni–B_4C (2), Ni–Al_2O_3 (3) and Ni–SiC (4). Potential scan rate 5 mV s^{-1}

evolution, remains actually unaffected by B_4C particles.

Thus, one can conclude that the increased corrosion susceptibility of Ni–B_4C composites should be ascribed to acceleration of a partial anodic reaction of the corrosion process, *viz*. nickel anodic dissolution. The entire system "MMC–corrosive environment" can be regarded as a system of interfaces "metal–particle–corrosive environment" and "metal–passive layer–corrosive environment" (the passive layer is commonly known always to be present on corroding nickel). It follows from the voltammetric measurements that the anodic activity of the metal–particle interface should be higher than the activity of the metal–passive layer interface. This conclusion is in harmony with the results of Al-MMC investigations conducted by Greene and Mansfeld [7]. The authors attributed the increased corrosion susceptibility of MMC to electrochemically active interfaces between the metal matrix and the reinforcement particles.

Voltammograms in Fig. 3 show that Al_2O_3 slightly inhibits the anodic dissolution in a neutral solution and actually does not affect the cathodic process. Slight inhibiting effects by Al_2O_3 and SiC on both anodic and cathodic partial processes are observed in acid solutions (Figs. 4 and 5).

Comparing data in Fig. 3 and Figs. 4 and 5, one can see that the currents in acid solutions are about one order of magnitude higher than those in the neutral solution. This implies much a higher coating activity in acid solutions.

In general, conclusions drawn from voltammetric measurements (Figs. 3–5) are in good agreement with those drawn from corrosion testing in salt fog (Figs. 1, 2). Indeed, when compared to pure nickel, both methods indicated a reduced corrosion resistance of Ni–B_4C, an increased resistance of Ni–Al_2O_3 and a significantly greater activity of coatings in the acid than in neutral environment.

The corrosion acceleration effect of B_4C was also studied by electrochemical impedance spectroscopy (EIS). Measurements were taken of both Ni and Ni–B_4C electrodes at the open circuit potential, and the results represented as Bode plots are shown in Fig. 6. No distinct differences were observed either in the shapes of impedance or phase curves of both specimens. This result leads to the conclusion that corrosion of pure Ni and Ni–B_4C occurs by the same electrochemical mechanism. The experimental data in Fig. 6 (symbols) were well fitted (lines) assuming the equivalent circuit, which consists of the solution resistance (R_Ω) and the charge transfer resistance (R) parallel with the constant-phase element (CPE) whose impedance is given by $Z_{CPE} = 1/C(j\omega)^{-n}$. The constant-phase element was used instead of the ideal capacity in order to take into account the capaci-

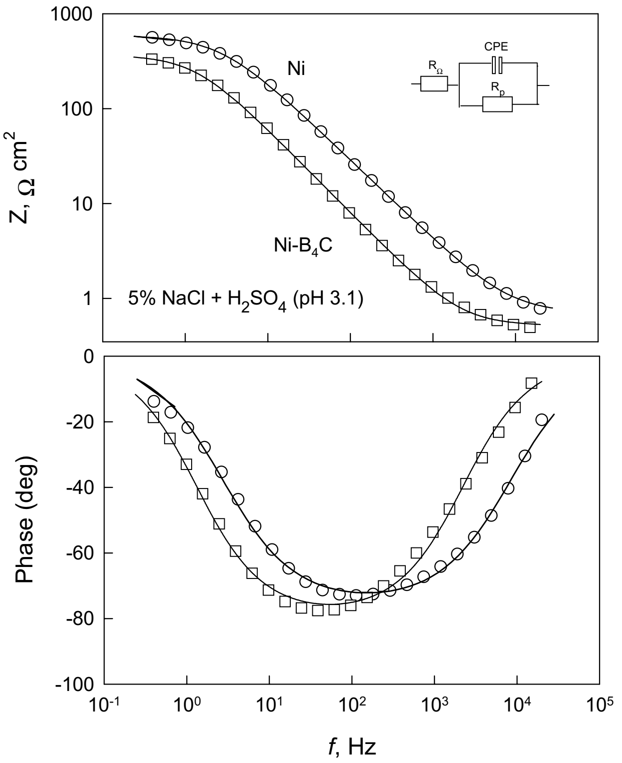

Fig. 6. Impedance spectra for Ni and Ni–B_4C in 5% NaCl + H_2SO_4 (pH 3.1). The symbols represent experimental data, and lines are fitting the results obtained assuming the equivalent circuit, which consists of the solution resistance R_Ω and polarization resistance R_p in parallel with the constant phase element (CPE). Fitting parameters for Ni: R_Ω = 0.7 Ω cm^2, R_p = 600 Ω cm^2, C = = 38 µF cm^{-2} (exponent in CPE 0.84). Fitting parameters for Ni–B_4C: R_Ω = 0.5 Ω cm^2, R_p = 370 Ω cm^2, C = = 154 µF cm^{-2} (exponent in CPE 0.89)

tance of the space charge within the passive film on nickel [16].

The impedance at a low frequency end of the spectrum ($Z_{f\to 0}$) is usually interpreted as the polarization resistance (R_p), which is inversely proportional to the corrosion rate [17, 18]. Impedance values in the low frequency domain are higher for pure Ni than for the Ni–B_4C composite (Fig. 6). Thus, the impedance of the Ni electrode at f = 0.01 Hz is Z = 650 Ω cm^2, whereas the analogous value for Ni–B_4C is Z = 370 Ω cm^2. Hence, impedance measurements once again confirm the corrosion resistance of Ni–B_4C to be less than that of pure nickel.

It should also be noted that the EIS data for other MMC were similar to the data in Fig. 6 and therefore are not presented in the paper.

CONCLUSIONS

Corrosion of Ni-MMC containing B_4C, Al_2O_3 and SiC has been studied in neutral and acid salt fog. Likewise, the electrochemical behavior of MMC has been investigated in neutral and acid solutions by means of voltammetry and impedance spectroscopy. In neutral salt fog, corrosion rates of Ni–Al_2O_3 and Ni–SiC did not differ significantly from those of pure nickel, whereas Ni–B_4C exhibited a significantly higher corrosion susceptibility. In the acid environment B_4C also accelerated corrosion, whereas Al_2O_3 tended to inhibit it.

It was concluded from voltammetric measurements that the corrosion susceptibility of Ni–B_4C composites increased due to acceleration of a partial anodic reaction of the corrosion process. The accelerated anodic dissolution of nickel was accounted for by a higher activity of the "metal/particle" interface than that of the "metal/passive layer" interface.

Reiceived 18 October 2001
Accepted 8 November 2001

References

1. A. Hovestadt and L. I. J. Janssen, *J. Appl. Electrochem.,* **25,** 519, (1995).
2. ICCE/7 Seventh Annual International Conference on Composites Engineering, Ed. D. Hui, 2000, Denver, Colorado.
3. K. A. Lucas and H. Clarke, Corrosion of aluminum-based metal-matrix composites. Research Studies Press, Ltd., 1993.
4. P. P. Traszkoma, E. M. McCafferty and C. R. Crowe, *J. Electrochem. Soc.,* **130,** 1804 (1983).
5. F. Mansfeld and S. L. Jeanjaquet, *Corros. Sci.,* **26**, 727 (1986).
6. S. Lin, H. Greene, H. Shih and F. Mansfeld, *Corrosion,* **48**, 61 (1992).
7. H. J. Greene and F. Mansfeld, *Corrosion,* **53**, 920 (1997).
8. C. Chen and F. Mansfeld, *Corros. Sci.,* **39**, 1075 (1997).
9. L. Benea, *Proceedings of the Symposium on Passivity and Breakdown*, Electrochem. Soc. Inc. Pennington, **97/26**, 981 (1998).
10. L. M. Yagodkina, I. D. Loginova, I. E. Savochina, *Russ. J. Appl. Chem.,* **70**, 1556 (1997).
11. G. N. K. Ramesh Bapu, *Plating,* **82**, 70 (1995).
12. V. Medelienė, K. Leinartas and E. Juzeliūnas. *Protection of Metals,* **31**, 98 (1995).
13. V. Medelienė, K. Leinartas and E. Juzeliūnas. *Chemija,* **4**, 25 (1996).
14. International Standard ISO 9227: Corrosion Test in Artificial Atmospheres – Salt Spray Test, Geneva, 1990.
15. International Standard ISO 8407: Corrosion of Metals and Alloys – Removal of Corrosion Products from Corrosion Test Specimens, Geneva, 1991, 1st ed.
16. J. R. Macdonald, in *Impedance Spectroscopy*, Wiley-Interscience, New York, 1987.
17. C. Gabrielli, Electrochemical Impedance Spectroscopy: Principles, Instrumentation, and Applications. In:

Physical Electrochemistry, ed. I. Rubinstein, Marcel Dekker, Inc, 243 1995.

18. M. Stern and A. L. Geary, *J. Electrochem. Soc.,* **104**, 56 (1957).

M.Gladkovas, V. Medelienė, M. Samulevičienė, E. Juzeliūnas

ELEKTROLITIŠKAI NUSODINTŲ KOMPOZITŲ NIKELIO METALO MATRICOS PAGRINDU SU B_4C, AL_2O_3 IR SIC INTARPAIS KOROZIJOS TYRIMAS

Santrauka

Pagreitintu korozijos testavimo būdu neutralioje ir rūgščioje druskos migloje buvo tiriama kompozitų nikelio metalo matricos pagrindu su B_4C, Al_2O_3 ir SiC intarpais korozija. Voltamperiniu ir pilnutinės varžos spektroskopijos metodais neutralioje ir rūgščioje terpėse buvo tiriama šių kompozitų elektrocheminė elgsena. Nustatytas B_4C dalelių akseleruojantis poveikis korozijai abiejose – neutralioje ir rūgščioje terpėse. Al_2O_3 dalelės stabdo koroziją rūgščioje ir neturi įtakos jai neutralioje terpėje. Remiantis voltamperometriniais matavimais, daroma išvada, kad Ni-B_4C kompozitų didesnis jautrumas korozijai yra dėl pagreitėjusios parcialinės anodinės reakcijos fazių metalas–dalelės sąlyčio riboje, palyginti su likusiu paviršiumi. Pirnutinės varžos spektroskopiniai matavimai neparodė esminių gryno Ni ir kompozitų elektrocheminio korozijos mechanizmo skirtumų.