Codeposition of SiC particles with cobalt matrix

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ABSTRACT

Purpose: The aim of this work was to determine the influence of current density and SiC powder concentration in the bath on the kinetics of the cathodic reaction as well as composition, morphology, microhardness and corrosion resistance of Co/SiC composite coatings.

Design/methodology/approach: Co/SiC composite coatings were deposited from a chloride-sulfate bath at two current densities (0.5 and 1 A/dm^2) and various SiC powder concentrations (10-50 g/dm^3). SiC content in the composites was determined by an image analysis. The microstructure was studied using optical and atomic force microscopes. Microhardness and corrosion resistance (in H_2SO_4) of the deposits were determined as a dependence on the SiC content in the coatings.

Findings: SiC incorporation increased (15-36 vol%) under powder addition to the bath, but increase in the current density enhanced cobalt matrix deposition. The last one resulted in lower particles contents in the coatings accompanied by an increase in the current efficiencies. Microscopic observations of the coatings revealed uniform distribution of the particles within matrix. Microhardness of the composites was 200-280 HV. Corrosion resistance of the coatings was improved a little at higher SiC content in the composites.

Practical implications: The paper describes the possibilities of codeposition of SiC particles with cobalt matrix.

Originality/value: The results of studies and conclusions presented in the paper are consecutive data complementing knowledge on codeposition of ceramic particles with cobalt.

Keywords: Electrodeposition; Composite; Silicon carbide; Cobalt

1. Introduction

Codeposition of various ceramic particles with a metal during electrolysis has been developed for industrial applications [1, 2]. Most of the research studies have been focused on the nickel matrix composites [1, 3], whereas other metals were studied in a lesser extent. Cobalt-base coatings can offer comparable or even better properties (hardness, strength and abrasion resistance) than nickel composites, especially for uses at elevated temperatures [4]. The review of the literature data shows that only several attempts on the codeposition of ceramic particles with electrolytic cobalt were performed. Carbides (SiC [5-7], Cr_3C_2 [8]), oxides (Cr_2O_3 [9], ZrO_2 [10], TiO_2 [11], lanthanide oxides [12, 13])

or nitrides (Si$_3$N$_4$ [14-16], BN [17]) were used in such studies. In comparison to the data on nickel composites, information on the cobalt coatings seems to be still poor. Hence, the aim of this work was to give further insights into the process of SiC codeposition with cobalt. The amount of embedded phase in the composite depends on the type bath-metal-particle combination and is governed mainly by the powder concentration in the plating bath, current density and agitation rate [1, 2]. This study was focused on the determination of the influence of the powder concentration in the bath at two current densities on the composition and some properties of Co/SiC composite layers.

2. Experimental procedure

Cobalt composites were deposited from solution containing: 15 g/dm^3 CoSO$_4$·7H$_2$O, 110 g/dm^3 CoCl$_2$·6H$_2$O, 25 g/dm^3 H$_3$BO$_3$ and 1 g/dm^3 saccharin. Suspensions contained α-SiC technical powder with concentrations of 10-50 g/dm^3. A mean size of the particles was approx. 4 μm. To wet and suspend uniformly the particles in the electrolyte, the suspension was agitated with a mechanical stirrer for about 1 hour before the electrolysis. The plating bath with the volume of 1 dm^3 was agitated with a magnetic stirrer with a rotation rate of 400 rpm and peristaltic pump with a circulation rate of 7.3 dm^3/h. Two fluxes of the suspension were flowed from the anodes to the cathode direction. Stainless steel plates as cathode substrates and two cobalt anodes were used. The anodes were placed symmetrically on both sides of centrally located cathode. All electrodes were in a vertical position in the cell. Before experiments the cathode substrate was cleaned with a grinding papers (400, 600, 800), washed with water and acetone. The pH of the bath was monitored with a pH-meter and the constant pH value (4.42 ± 0.02) of the bath (which showed a tendency to alkalization due to hydrogen evolution) was maintained by periodic addition of drops of a mixture of diluted HCl and H$_2$SO$_4$ acids. Electrodeposition runs were carried out for 8 hours at two current densities of 0.5 A/dm^2 and 1.0 A/dm^2. In order to determine the charge flowed through the circuit, the copper coulometer was connected to the cathode. The mass gains of the cathodes in the electrolyser and coulometer were determined gravimetrically. Cathodic potential was measured versus saturated calomel electrode and then referred to the normal hydrogen electrode. The morphology of as-plated and polished deposits was examined by means of optical and atomic force microscopes. SiC contents in the composites were determined by image analysis (Aphelion program) using photographs (optical microscope) of polished samples. Microhardness of the deposits was determined on the surface of the composite layers at the loading of 100g (Hanemann hardness tester). Corrosion resistance of the deposits was determined in 10% H$_2$SO$_4$ at room temperature. A three-electrode cell, consisting a Co/SiC electrode with an exposed area of 2 cm^2 as working electrode, an Ag/AgCl electrode as reference electrode and a platinum plate as a counter electrode, was used. Linear sweep voltammograms were recorded in the potential range from -1000 mV to 500 mV (vs Ag/AgCl) at the scan rate of 10 mV/s using Atlas Sollich 98 EII potentiostat. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1a shows galvanostatic polarization curves registered in the baths with various SiC concentrations. It was found that the presence of the powder shifts the curves towards more negative potentials. This effect was more evident for SiC concentrations up to 20 g/dm^3, whereas at higher contents of the powder in the suspension the course of the curves was not affected significantly by the particles. The cathode potential registered at $i = 0$ was –0.191 ± 0.008 V. It corresponded with a corrosion potential, since equilibrium value calculated from Nernst equation for Co/Co^{2+} electrode is –0.286 V for Co^{2+} concentration used in this study.
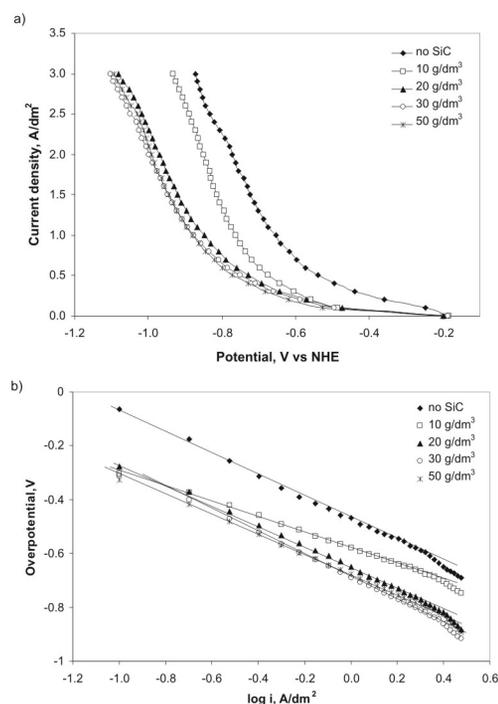

Fig. 1. Influence of SiC concentration in the bath on the polarization curves

The polarization curves plotted in the Tafel coordinates showed linear dependencies of the overpotential on the logarithm of the current density (Fig. 1b). It shows that electron transfer was the rate-determining step of the cathodic process for all cases. It was interesting that the linear range was extended for the currents densities up to approx. 2.5 A/dm^2 in the presence of the powder, while the linear plot below 2.2 A/dm^2 for pure cobalt deposition was found. It suggests that ceramic particles can enhance transport of metallic ions to the electrode (previous studies [7] showed that 1 g SiC can adsorb approx. 0.02 mg Co^{2+}). At higher current densities the rates of the electron transfer and transport of cobalt ions to the cathode became comparable and some deviations from the linearity appeared. The slopes of the straight lines were high (0.37 ± 0.04 V/dec) and different from theoretical value for cobalt (0.059 V/dec for α = 0.5). It is known that accurate determination of the Tafel slopes requires linear relationships in the current range of two current decades at least.

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This requirement could not be realized in this study, since deposits cracked spontaneously and separated from the substrate at the current densities over 3 A/dm^2. Despite of that it is worth to note that high slopes are rather characteristic for cobalt or nickel deposition process [7, 18].

Co/SiC composites were deposited at two current densities. The currents were rather low (0.5 and 1 A/dm^2) to ensure that the cathodic process was under activation control. Fig. 2 shows the influence of the powder concentration in the suspension on the SiC content in the composite. It was found that incorporation of the particles increased with increased SiC content in the bath. However, at higher current density lower contents of the particles were found in the deposits. It shows that increase in the current density can increase the rate of metal deposition, but it does not affect on the rate of the particles incorporation since the latter is dependent mainly on the hydrodynamic conditions in the electrolyser.
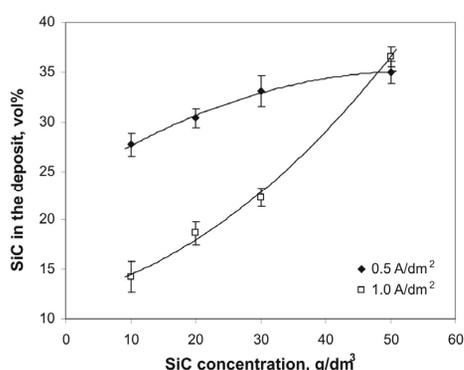

Fig. 2. Influence of the powder concentration in the bath on the SiC content in the composites

Fig. 3 shows changes of the current efficiency on the electrolysis conditions. The values were calculated for only reduction of cobalt ions since SiC particles do not participate in the electrode reaction:

$$\eta_{\%} = \frac{m_{Co}}{k_{Co} I t} \cdot 100\% = \frac{m_{Co/SiC} - m_{SiC}}{k_{Co} I t} \cdot 100\% \qquad (1)$$

where: $\eta_{\%}$ – current efficiency, $m_{Co/SiC}$, m_{Co}, m_{SiC} - mass of the composite, cobalt matrix and SiC in the composite, respectively, k_{Co} – electrochemical equivalent of cobalt, I – current intensity and t – electrolysis time. Mass of the composite deposit $m_{Co/SiC}$ was determined gravimetrically, while mass of SiC incorporated was calculated on the volume content of the particles in the deposit, according to the equation:

$$m_{SiC} = \frac{m_{Co/SiC} \cdot \alpha \cdot d_{SiC}}{\alpha \cdot d_{SiC} + (1-\alpha) \cdot d_{Co}} \qquad (2)$$

where: α – volume fraction of SiC in the deposit, d_{SiC}, d_{Co} – density of SiC and cobalt, respectively.

Current efficiencies were relatively low values and reached approx. 88-95 %. It was interesting that for both current densities maxima appeared on the curves. The maximum was shifted towards lower concentrations of the powder at higher current density. It is understandable, since higher current efficiencies were reached for lower SiC contents in the deposits (Fig. 3b). This phenomenon is consistent with the polarization data as particles embedded in the matrix change the cathode area and the actual cathodic current density. The SiC inclusions can block the working cathode surface and thus inhibit deposition of the metal. This statement seems to be understandable due to lower conductivity of α-SiC (7.7·10^2 S/m) in comparison with the value for cobalt (1.8·10^7 S/m) [19]. The particles' conductivity is five orders of magnitude lower than that for the matrix and SiC particles in cobalt can be considered as "non-conducting" inclusions. Moreover, Watson [20] found that SiC particles can transport adsorbed hydrogen ions to the electrode surface, where are reduced in the cathodic process. It was confirmed by Hwang and Hwang [5], who found that at low current densities (below 2 A/dm^2) the rate of particle deposition was mainly determined by the reduction of H$^+$ ions adsorbed on SiC.
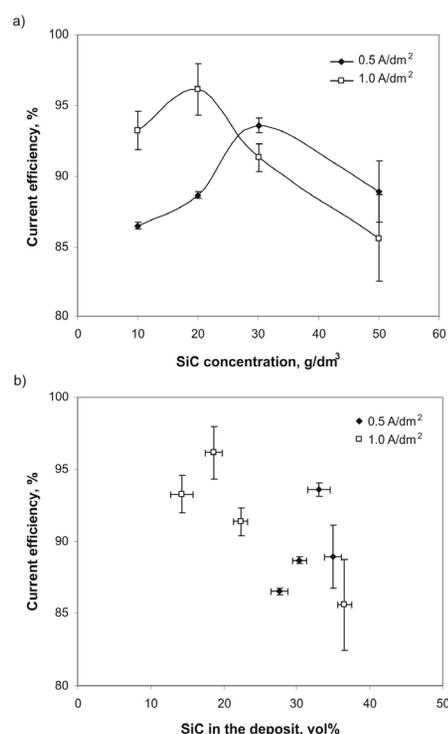

Fig. 3. Dependence of the current efficiency on: a) SiC concentration in the bath; b) SiC content in the composite

Fig. 4 shows polished sample of the Co/SiC composite. The particles were uniformly distributed within the matrix. There were not any places (e.g. pit edge) of the preferential incorporation of the particles as it was observed previously for the composites obtained in the presence of Cs$^+$ ions [7].
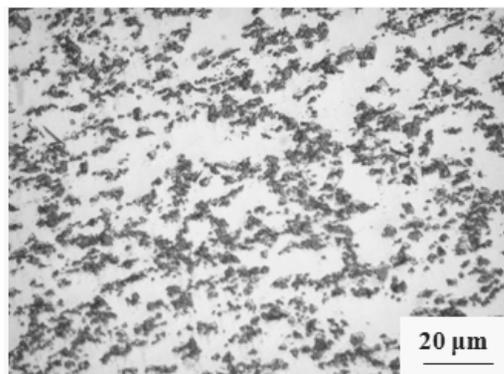
Fig. 4. Distribution of the particles within the Co/SiC composite (1 A/dm^2, 50 g/dm^3 SiC)

Fig. 5 shows details of the surface structure of the cobalt matrix observed by means of AFM microscope. Metallic matrix characterized by needle-like microcrystallite structure characteristic for cobalt electrolytic deposits with hexagonal crystallographical system.
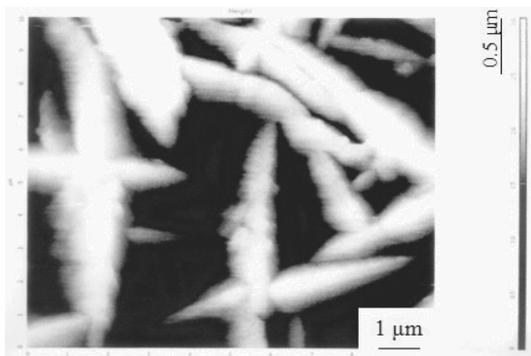

Fig. 5. Surface morphology of the cobalt matrix

The dependence of the composite microhardness on the SiC content in the deposit is presented in Fig. 6. It was found that the microhardness increased from approx. 200 HV for 14 vol% SiC up to approx. 280 HV for 35 vol% SiC. The effect of the current density on the matrix microhardness can not be neglected, since even at low current densities the size of the metal grains can differ. It is visible for the composites deposited at 1.0 A/dm^2 and 0.5 A/dm^2 and containing 14 vol% and 27 vol% SiC, respectively. They characterized with similar microhardness, even though the SiC fractions in the composites varied significantly. However, results for every tested coating were characterized by quite wide scatter of data (up to ± 50 HV). This effect can be related to locally varied distribution of hard SiC particles in the microareas and positioning of the microindenter on the material surface.

Corrosion resistance of Co/SiC coatings was also tested. Table 1 summarizes exemplary data registered in H$_2$SO$_4$ solution. It was found that the increased SiC content in the composites

improved somewhat corrosion resistance of the deposits, but it was better for the coatings obtained at lower current density. It suggests that decrease in the corrosion currents at higher amounts of particles embedded in the matrix was probably due to semiconducting properties of silicon carbide and, hence, less tendency for formation of galvanic cells in uniform cobalt matrix.
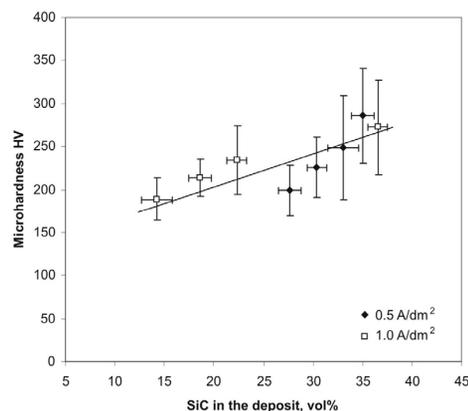

Fig. 6. The influence of SiC content in the deposit on the composite microhardness

Table 1.
Corrosion currents and potentials of Co/SiC composites deposited at 1 A/dm^2

SiC concentration in the bath, g/dm^3	SiC content in the composite, vol%	Corrosion current density, µA/cm^2	Corrosion potential, mV vs Ag/AgCl
10	14.2	255	-280
20	18.7	251	-270
30	22.3	200	-260
50	36.5	198	-260

4. Conclusions

Co/SiC composite layers were produced by the electrodeposition from the Watt's-type bath. SiC incorporation increased under powder addition to the bath, but increase in the current density enhanced cobalt matrix deposition. The last one resulted in lower particles contents in the coatings accompanied by increase in the current efficiencies. Microscopic observations of the coatings revealed uniform distribution of the particles within matrix. Microhardness of the composites was 200-280 HV, however, a wide scatter of data related to locally varied distribution of SiC particles in the microareas was observed. Corrosion resistance of the coatings was improved by increased SiC content in the composites due probably to less receptivity for formation of galvanic cells in the matrix in the presence of low conducting ceramic inclusions.

Acknowledgements

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