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INFLUENCE OF ELECTROLYSIS PARAMETERS ON THE CONTENT OF DISPERSION PARTICLES IN Co-SiC COMPOSITES

WPLYW PARAMETRÓW ELEKTROLIZY NA ZAWARTOŚĆ CZĄSTEK DYSPERSYJNYCH W KOMPOZYCIE Co-SiC

The influence of cathodic current density and concentration of dispersed particles in the bath on SiC content in Co-SiC composites was studied. The particles' presence resulted in the inhibition of the cathodic process, which slowest stage was charge-transfer step. The volume fraction of the strengthening phase in the coatings was 5-28% and it was dependent on the electrolysis conditions. The fraction of particles in the matrix was determined by the rate of cobalt deposition and the rate of particle deposition – maximum SiC contents in the composite were obtained when $V_{SiC} > 0.1V_{Co}$.

Przeprowadzono badania wpływu katodowej gęstości prądu oraz stężenia cząstek dyspersyjnych w kąpeli na udział fazy umacniającej w kompozycie Co-SiC. Obecność cząstek prowadzi do zmniejszenia hamowania procesu katodowego, którego najwolniejszym etapem jest reakcja przejścia. Udział fazy umacniającej w powłoce wynosi 5-28%obj. i zależy od warunków prowadzenia elektrolizy. Udział cząstek w osnowie jest uwarunkowany przez szybkość osadzania kobaltu oraz szybkość osadzania cząstek – maksymalne zawartości SiC w kompozycie uzyskano, gdy $V_{SiC} > 0,1V_{Co}$.

1. Introduction

Cobalt matrix coatings occupy an important place among metal/ceramics composites that are produced by electrolytic method. Despite the fact that cobalt and nickel properties are similar an enormous amount of research work is devoted only to nickel composite coatings, strengthened in particular with silicon carbide particles [1, 2]. This has contributed to the wide industrial application of nickel composites from early 1970s, while the possibilities brought by the cobalt matrix are not yet fully used. For example, at elevated temperatures the cobalt composites frequently show much higher hardness, strength and wear resistance in comparison to nickel matrix coatings [3, 4]. Because of that Co-Cr₃C₂ composites [5] are now being used to produce aircraft and rocket engine parts, while Co-ZrO₂ [4] – in the automotive, aircraft and armaments industries. Co-Si₃N₄ coatings [6] are used to produce cutting tools, turbine blades, borers and drills.

Relatively limited information on electrolytic cobalt composite coatings can be found in the literature. The

largest number of research papers was published by a group of Indian scientists: Rajiv, Iyer, and Seshadri [4, 6-10]. Their interests comprised composite coatings strengthened with various particles: silicon nitride [6-8], zirconium oxide [4], titanium oxide [9] and cerium oxide [10]. This research group carried out fundamental studies related to the influence of a number of different parameters (e.g. current density, pH, stirring rate, concentration of the dispersed particles in the bath) on the codeposition [7], as well as research on tribological properties [4, 8] and the corrosion resistance of cobalt composite coatings [6, 9, 10]. Similar measurements were also performed during cobalt matrix codeposition with other particles: boron nitride [11], lanthanides oxides (CeO₂, La₂O₃, Nd₂O₃, Y₂O₃) [12], chromium oxide [3] or silicon carbide [13, 14]. The authors [13] described also a theoretical model of particles codeposition with a metallic matrix. The model considered the influence of H⁺ and Co²⁺ ions adsorbed on the particles on the SiC codeposition rate at various current densities and particle concentrations in the bath.

Zhang et al. [15] proposed a specific application of

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the electrolytic cobalt codeposition with ceramic particles. The authors carried out two-stage electrolysis in order to obtain Co-hydroxyapatite coating, which can be potentially applied as for materials used in production of implants.

Despite of sufficient knowledge, the work on the optimisation of silicon carbide particle codeposition with metallic matrix, in particular with the nickel matrix, is still in progress. Less attention is devoted to cobalt composites. Hence, the aim of the present study is determination of the influence of electrolysis parameters on SiC particles codeposition with this metal.

2. Experimental

The codeposition of cobalt with SiC particles was carried out in a chloride-sulphate bath at pH 4.4. Its composition was: 200 g/dm³ CoCl₂·6H₂O, 25 g/dm³ CoSO₄·7H₂O, 25 g/dm³ H₃BO₃, 1g/dm³ of saccharine, and various concentrations of SiC: 5, 10, and 20 g/dm³. The average size of the SiC particles was approx. 5 μm. Analytical purity reagents and technical SiC powder were used. The measurements were carried out in a cubical PVC vessel, containing 2 dm³ of the suspension. To reduce the sedimentation of the SiC particles in the electrolyser, the bath was circulated by means of two peristaltic pumps at a flow rate of approx. 4.6 dm³/h each. Stirring by means of a magnetic stirrer with a rotation rate of 150 rpm was applied additionally. In order to break up the SiC agglomerates, the suspension was vigorously stirred with a mechanical stirrer (900 rpm) for 1 h before each electrolysis. A cathode (5 × 5 cm) made of stainless steel was located in the centre of the electrolyser between two cobalt (99%) anodes. Before each measurement, the cathode plate was cleaned with abrasive papers, etched in a nitric acid solution, and then washed in distilled water and acetone.

Cathodic polarisation curves were registered under galvanostatic conditions in baths with various SiC contents. Prior to each measurement, a layer of composite was electrodeposited for 1 h at the current density of 1 A/dm².

The electrolyses were carried out at various current densities in a range of 0.5-2.0 A/dm². The bath's pH was continuously controlled by means of a pH-meter and adjusted to 4.4 by adding a mixture of HCl + H₂SO₄ acids (1:1). The cathode potential was continuously measured against a saturated calomel electrode and then calculated against the normal hydrogen electrode (NHE). 5 cm³ samples of the electrolyte were taken at various interval during the electrolysis to determine the concentration of Co²⁺ ions (titration with 0.1 M EDTA using murexide as the indicator).

A copper coulometer was incorporated in series in the circuit to determine the cathode efficiency. The mass of the composite deposits was determined gravimetrically. Microscopic observations (optical microscope NEOPHOT) of the composite surface were performed. The cathodic deposits (separated from the steel substrate) were polished with abrasive papers and then in a polishing machine with the use of Al₂O₃ suspension. Micrographs of the composites were analysed using Aphelion (ADCIS&AAI) software in order to determine the volume fraction of SiC particles in the composites. The structure of the cathodic deposits was also studied by means of a transmission electron microscope (JEM 2010ARP).

3. Results and discussion

Fig. 1 shows the cathodic polarisation curves recorded in the baths containing 5, 10, and 20 g/dm³ of SiC. It was observed that the changes in the SiC particle concentration in the bath were accompanied by changes in the cathode polarisation – the cathodic overvoltage decreased with the increase of the amount of powder in the electrolyte. The results obtained are different from that reported by Hwang and Hwang [13], who found no effect of the SiC concentration (0 – 5 g/dm³) on the course of the cathodic polarisation curves during the cobalt deposition. On the other hand, in the case of SiC codeposition with the nickel matrix [16], the inhibition of the cathodic process declined with increased content of the particles in the electrolyte.

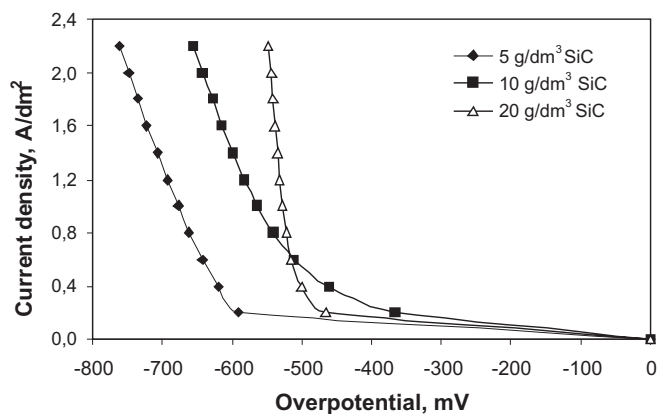


Fig. 1. The influence of SiC concentration in the bath on the course of the cathodic polarization curves

It is noteworthy that in the absence of current flow from an external source ($i = 0$), the potential of an electrode did not correspond with the value of the equilibrium potential ($E_o = -278$ mV for 0.93 M Co²⁺ in the bath). For the SiC concentrations 5, 10, and 20 g/dm³,

these were: -8, -157 and -162 mV (against NHE), respectively, and corresponded with the corrosion potentials. It is also noteworthy that in the case of higher SiC concentrations in the suspension (10 and 20 g/dm³), the values of the corrosion potentials as well as the volume fractions of SiC in the composites (Fig. 6) were similar, while for 5 g/dm³ SiC these values were different. Therefore, the change of the corrosion potential towards more electronegative values (towards equilibrium potential) with an increasing SiC contents in both the bath and the cathodic deposits suggested that the SiC presence in the coating resulted in higher corrosion resistance of the composites in comparison with the pure matrix. This trend is consistent with the data found in the literature, which indicated a decline in the corrosion current (in NaCl solutions) of cobalt coatings strengthened with various particles: Si₃N₄ [6], TiO₂ [9], and CeO₂ [10, 12]. On the other hand, the presence of lanthanide oxide particles (except for CeO₂) deteriorates the corrosion resistance of cobalt coatings [12].

Fig. 2 shows the dependence of cathode overvoltage η on $\log i$. Despite of rectilinear relationships in the Tafel coordinate system, it was difficult to draw conclusions about the process mechanism. The process seems to proceed in the activation area, i.e. the charge-transfer stage of Co²⁺ reduction is a rate-determining step. For 5 g/dm³ SiC, it seems that at higher current density a deviation from linearity occurs and the process may then proceed in the area of mixed control. However, the slopes of straight lines have values that are clearly different (-162, -250, and -60 mV/dec at increasing SiC concentration) from the theoretical values (-59 mV/dec for $\alpha = 0.5$). The fundamental reason is the fact that polarisation curves were registered in excessively narrow ranges of current density. The correct determination of the slopes requires a rectilinear relationship $\eta = f(\log i)$ at least within two current decades. In the present study, the cathodic polarisation curves were registered in a narrow range of current density – only up to 2 A/dm². The preliminary trials of cathodic cobalt codeposition with SiC particles have shown that above this current density the cathodic deposits were spontaneously breaking and separating from the plate already during the electrolysis. Therefore, it is advisable to deposit the Co-SiC coatings at current densities below 2 A/dm². On the other hand, the fact that the registration of the polarisation curves starts from the corrosion, not equilibrium, potentials substantially narrows the range of rectilinear Tafel's relationship (in the low current density range), and thereby affects the correctness of the rectilinear range determination.

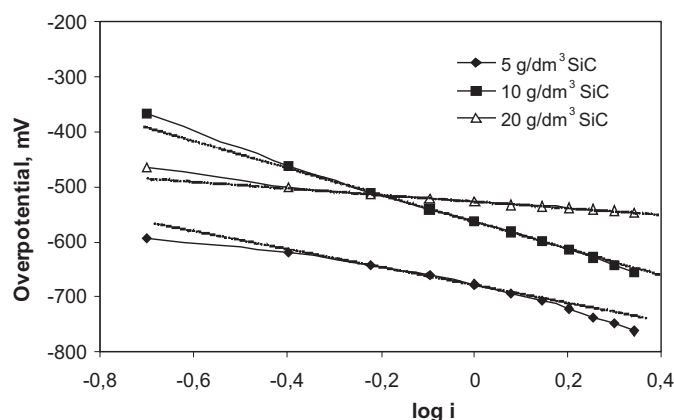


Fig. 2. The cathodic polarization curves in the Tafel coordinate system

Cathode potential versus time was registered for each measurement. It was observed that irrespective of the dispersive particles' content in the bath, a general regularity was valid, i.e. at higher current densities the potential values became more electronegative, which is equivalent to the higher polarisation of the cathode. Fig. 3 shows examples of the relationships for the series of measurements carried out in the bath containing 10 g/dm³ SiC. It is noteworthy that the values of the potential for $t = 0$ corresponded with the potential of the polarised steel substrate.

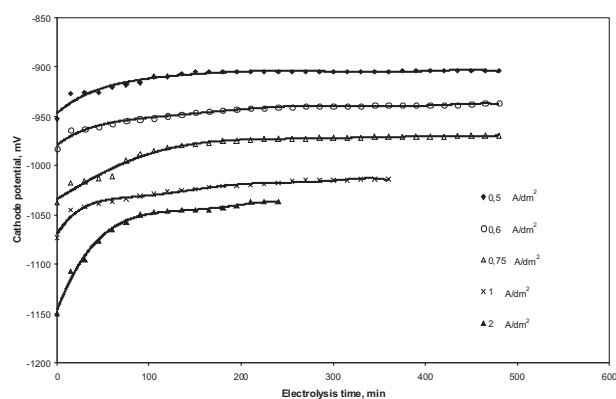


Fig. 3. The influence of the electrolysis time on the cathode potential (10 g/dm³ SiC)

Cathodic efficiencies were calculated basis of on the increments in the mass of the cathodes in the electrolyser and coulometer. Fig. 4 shows the results versus the applied current densities and the particle concentrations in the bath. It was found that the codeposition of Co-SiC composites characterized with rather high current efficiencies: 97.5-99.9%. However, these values were slightly overestimated because the mass of the SiC particles in the composite was not considered in the calculations. However, the error resulting from this approximation is small due to the much lower SiC density compared with

the matrix metal density and relatively low content of SiC particles in the composites (maximum: 28.5 vol%, i.e. 12.5 wt.% SiC).

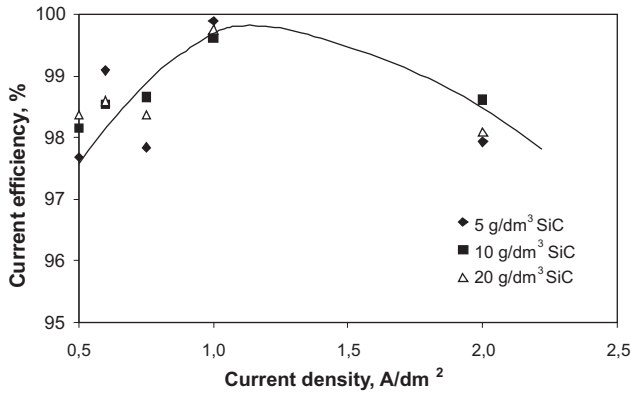


Fig. 4. The influence of the current density and SiC concentrations in the bath on the current efficiency

The concentration of Co^{2+} ions was determined at various intervals during the electrolysis. Irrespective of the current density used or the particles content in the bath, the concentration of cobalt ions in the baths remained at a constant level of $0.93 \pm 0.03 \text{ M}$.

The particle volume fractions in the composites were determined on the analysis of the microstructure's image, obtained by means of an optical microscope. Fig. 5 shows the dependence of the particle volume fraction in the composites on the current density and on the particle concentration in the bath. From the literature data [7, 12, 13], it is known that for higher particle concentrations the bath, higher SiC fraction in the composite c_V are observed. For the examined Co-SiC system, this regularity is satisfied only for the composites obtained for three current densities: 0.5, 0.6, and 1.0 A/dm^2 . In the case of a bath containing 10 g/dm^3 of SiC, maximum is observed on the $c_V = f(i)$ curve at a current density of 0.75 A/dm^2 (27.2 vol.%). However, for a particle concentration of 20 g/dm^3 , the maximum of SiC content in the coating appears at two current densities of 0.5 and 1.0 A/dm^2 (28.5 and 24.6 vol.% of SiC, respectively). For 5 g/dm^3 of SiC in the electrolyte, the percentage content in the composite amounts to approx. 5 vol.%, where a weak maximum is noticeable at the current density of 0.75 A/dm^2 .

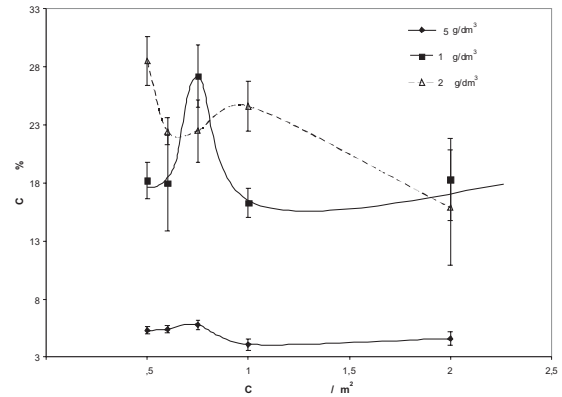


Fig. 5. The influence of the current density and SiC concentration in the bath on the SiC volume fractions in the composites

The occurrence of the maxima on the $c_V = f(i)$ curves for SiC concentrations of 2 – 10 g/dm^3 was observed by Hwang and Hwang [13]. The authors carried out studies within the current density range of 0.1 – 6 A/dm^2 in sulphate-chloride baths of pH 4.0 containing approx. 0.42 M Co^{2+} . Irrespective of the particle concentration in the suspension it was observed that, initially, with the current density increasing to 2 A/dm^2 , the SiC fraction in the cathodic deposit declined from the maximum value for 0.1 A/dm^2 . Furthermore, an increase in the current density to 4 A/dm^2 was accompanied by a rise in particles fraction, and once the maximum was passed, the content of the ceramic phase in the cathodic deposit fell again. To explain the relationships presented, a theoretical model was proposed, in which the occurrence of two limiting currents was considered – reduction of hydrogen ion and cobalt ion adsorbed on ceramic particles. The conclusion was that at low current densities the rate of particle deposition was mainly determined by the reduction of H^+ ions adsorbed on SiC, while at high current densities, the reduction of both ion types determined the rate of particles embedding into the cobalt matrix.

The results of the measurements performed in the study do not allow for the use of the model discussed above. This results from the fact that the studies were carried out with a narrower range of current density (limitations were related to the spontaneous cracking of coatings already during the deposition within a few-hours of the electrolysis). In addition, the maxima of the strengthening phase's content in the composite depended on the conditions of the process' running. However, in each case it may be assumed that the percentage (weight) fraction of the particles in the matrix c_m is conditioned by the rate of cobalt deposition V_{Co} and the rate of particles deposition V_{SiC} [13]:

$$c_m = \frac{V_{\text{SiC}}}{V_{\text{SiC}} + V_{\text{Co}}} \cdot 100\% \quad (1)$$

During the metallic layer growth, the Co^{2+} ions originating from the electrolyte as well as those adsorbed on SiC particles existing on the cathode's surface can reduce. However, it seems that the latter has relatively low contribution in the total process. From Fig. 2 it can be clearly seen that metal ion reduction proceeds in the area of activation control, therefore the cobalt deposition rate V_{Co} may be described by the equation:

$$V_{\text{Co}} = k \cdot i \cdot \eta_{\text{Co}} \quad (2)$$

where k – the cobalt electrochemical equivalent

i – the cathodic current density

η_{Co} – the current efficiency of cobalt deposition

Equation (2) shows a rectilinear dependence of the metal deposition rate on the current density. Fig. 6a shows experimental points (determined on the mass and composition of cathodic deposit) and straight lines resulting from equation (2). It has been found that irrespective of the SiC particle content in the bath, the matrix deposition rate is the same and corresponds with the quantity as determined by Faraday's law.

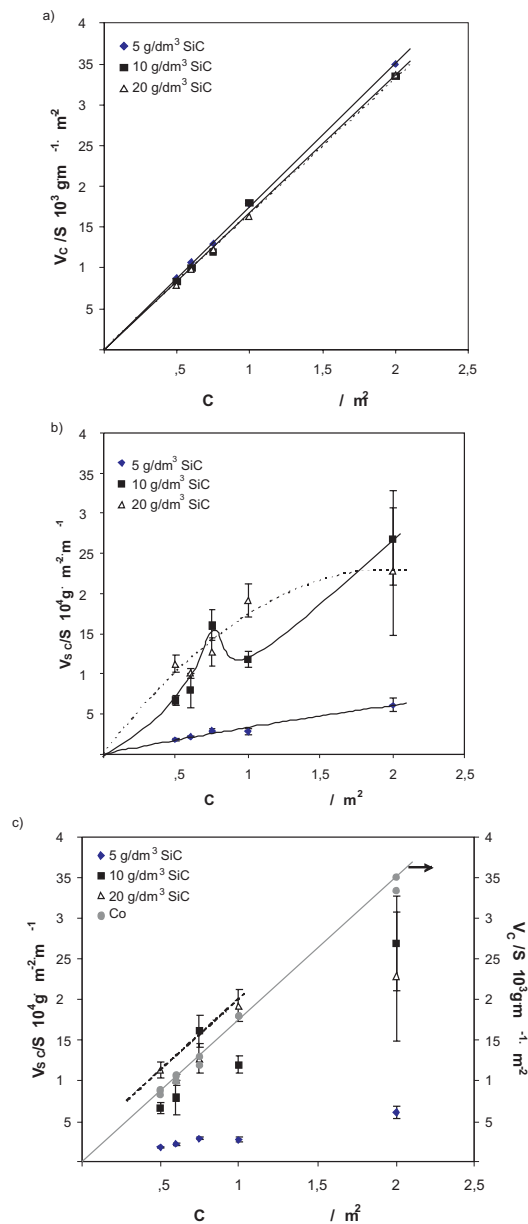


Fig. 6. The influence of current density on the Co and SiC deposition rates

The SiC particles deposition rate may be determined based on the cathodic deposit mass and particle volume fraction in the matrix:

$$V_{SiC} = \frac{m}{t \cdot S} \cdot \frac{c_V \cdot d_{SiC}}{c_V \cdot d_{SiC} + (100 - c_V) \cdot d_{Co}} \quad (3)$$

where m – the cathodic deposit mass
 t – the electrolysis time
 S – the cathode surface
 d_{SiC} – the SiC density (3.2 g/cm³)
 d_{Co} – the cobalt density (8.9 g/cm³)

The obtained results are shown in Fig. 6b as a function of the current density applied. It was found that the rate of the SiC particle embedding increased with increasing current density. This trend is consistent with the predictions of Kariapper and Foster [17], who suggested the following equation for the rate of particle embedding V_{cz} :

$$V_{cz} = \frac{N^*k \cdot c_V}{1 + k \cdot c_V} \quad (4)$$

where N^* – is the effective number of particle collisions with the cathode resulting in particle embedding in the matrix in a unit of time. This value depends on the circulation rate of the suspension. k – is the constant characteristic for the specific type of interactions between the particles and cathode surface. The value of constant k depends

mainly on the particle surface charge q , cathode potential E , cathodic current density i , area of the metal-particle interface L , and circulation rate M :

$$k = k * (qE + Li^2 - M) \quad (5)$$

According to the model presented by both authors, the maximum particle content in the matrix is achieved when the metal deposition rate is equal to the particle embedding rate at the current density i_m . This means that the slopes of the tangents to curves $V_{cz} = f(i)$ at point of i_m assume the same values as the slope of the straight line corresponding to the metallic matrix deposition. However, under experimental conditions, the metal deposition rate is by an order of magnitude higher than the rate of ceramic particle embedding (Fig. 6 a, b). This also means that the maximum SiC contents in the cobalt matrix may be expected when $V_{SiC} > 0.1V_{Co}$, then the value of c_m will be higher by 10% (Table). Fig. 6c compares V_{SiC} and V_{Co} values versus the current density. It was found that the maximum SiC content in the composite may be expected for the bath containing 10 g/dm³ SiC at the current density of 0.75 A/dm² and for the bath containing 20 g/dm³ SiC at the current densities of 0.5 and 1.0 A/dm². Moreover, it was noticed that the aforementioned three experimental points are situated on a straight line parallel to the line corresponding to the cobalt matrix deposition rate. Slopes of these straight lines are: $a_{SiC} = 1.6 \cdot 10^{-3}$ g/(min·A) and $a_{Co} = 16.6 \cdot 10^{-3}$ g/(min·A), respectively.

TABLE

Comparison of SiC and cobalt deposition rates

Current density, A/dm ²	SiC concentration in the bath, g/dm ³					
	5		10		20	
	$\frac{V_{SiC}}{V_{Co}}$	$\frac{V_{SiC}}{V_{SiC}+V_{Co}} \cdot 100\%$	$\frac{V_{SiC}}{V_{Co}}$	$\frac{V_{SiC}}{V_{SiC}+V_{Co}} \cdot 100\%$	$\frac{V_{SiC}}{V_{Co}}$	$\frac{V_{SiC}}{V_{SiC}+V_{Co}} \cdot 100\%$
0.5	0.02	1.97	0.08	7.41	0.14	12.54
0.6	0.02	2.01	0.08	7.32	0.10	9.33
0.75	0.02	2.17	0.13	11.86	0.10	9.45
1	0.02	1.51	0.07	6.54	0.12	10.51
2	0.02	1.70	0.08	7.45	0.07	6.36

Fig. 7 shows microstructures of surface microsections of the composites obtained from the baths of different SiC contents. It was found that the distribution of

dispersive particles in the matrix was uniform and their fraction in the composite was variable depending on the applied electrolysis parameters.

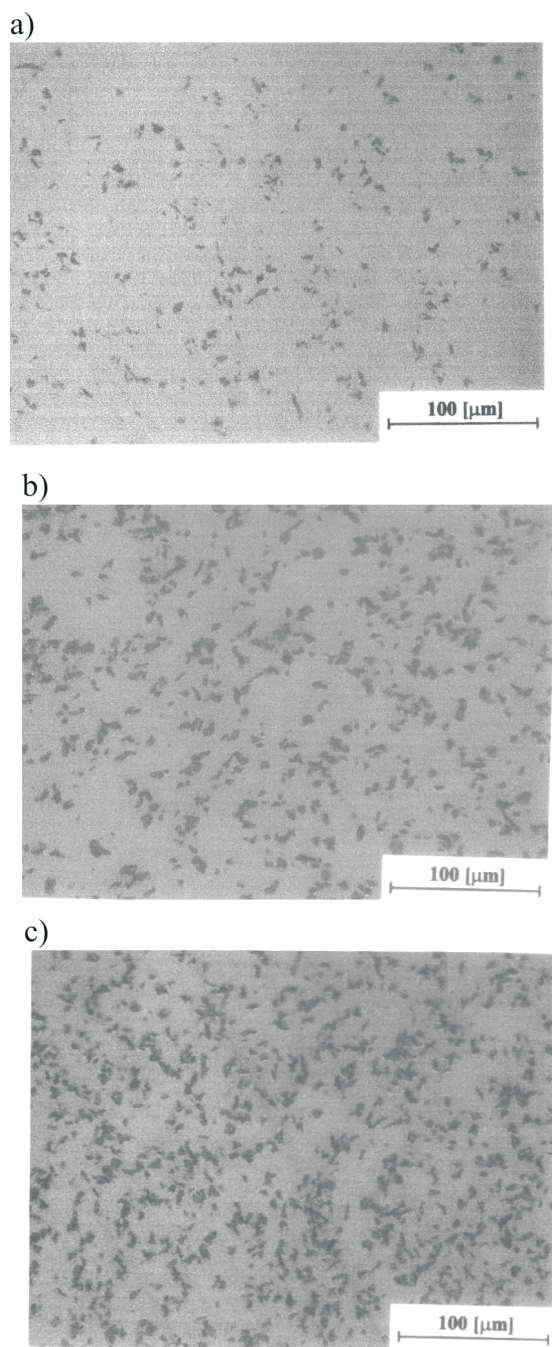


Fig. 7. Surface microsections of Co-SiC composites (1 A/dm^2) electrodeposited at various SiC concentrations: (a) 5 g/dm^3 , (b) 10 g/dm^3 , (c) 20 g/dm^3

The obtained composite coatings were observed by means of a transmission microscope. Fig. 8 shows micrographs of the Co-SiC specimen. It was found that SiC particles are rather precisely built-up by the metallic ma-

trix – edges of the particles are very clearly visible (Fig. 8a). Cobalt is deposited in turn creating characteristic elongated grains, (Fig. 8b). Such a structure is characteristic for cobalt coatings of a hexagonal structure.

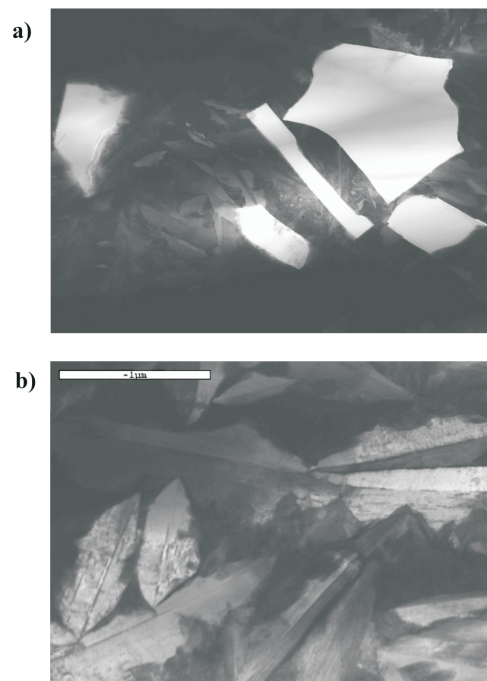


Fig. 8. TEM micrographs of Co-SiC composite: a) SiC particles in the matrix; b) the microstructure of cobalt matrix

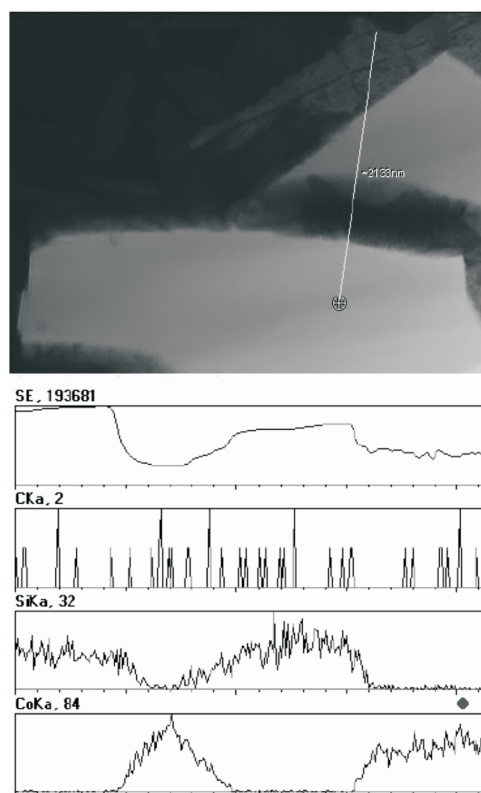


Fig. 9. Line analysis of Co-SiC composite

Figs. 9 and 10 present the results of an elemental analysis “along the line” and element distribution in the form of a “map”. It was found that a sudden change in the

cobalt and silicon content occurs on the particle-matrix interfaces, which is confirmed by the precise build-up of the strengthening phase particles by the metallic matrix.

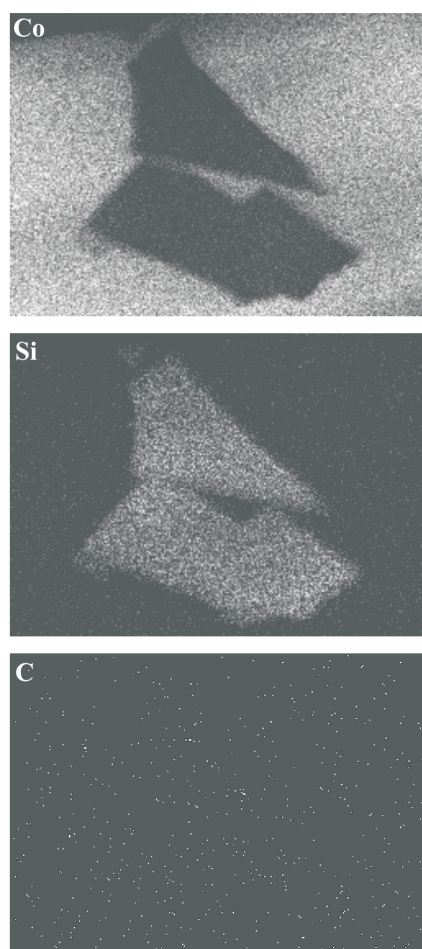


Fig. 10. STEM mapping of the Co-SiC composite

4. Conclusions

Cathodic cobalt codeposition with SiC particles allows for the production of good quality composite coatings. However, the process of electrolysis should be carried out under conditions of intensive suspension stirring and at current densities that do not exceed 2 A/dm^2 . It was found that the particles' presence in turn results in the reduced inhibition of the cathodic process, in which its slowest stage is the charge-transfer step. The fraction of the strengthening phase in the coating amounts to 5-28 vol.% and depends on the particle concentration in the bath as well as on the current density. The fraction of the particles in the matrix is conditioned by the rate of cobalt deposition and rate of particle deposition, in

which the maximum SiC content in the composite was obtained when $V_{SiC} > 0.1V_{Co}$.

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