

Corrosion behaviour of aluminium matrix composites reinforced with sintered halloysite nanotubes

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ABSTRACT

Purpose: The aim of this study was to determine the effect of mass fraction and sintering temperature of the halloysite nanotubes on the corrosion behavior of the infiltrated AISi12 matrix composites, concerning the matrix alloy.

Design/methodology/approach: The corrosion resistance research was done with a potentiodynamic method. Electrochemical corrosion research was made in water centre of 3% NaCl at room temperature. Electrochemical studies of corrosion resistance were performed by determine the open circuit potential and saving the anodic polarization curves by applying to potential changes in the direction of anode and cathode at 1 mV/s. Based on the registered anodic polarization curves were determined: corrosion potential, passive layer breakdown potential, corrosion current density, polarization resistance. The value of corrosion current was determined using the Tafel extrapolation.

Findings: Mass fraction of the halloysite nanotubes does not affect the corrosion resistance of the composites as opposed to their sintering temperature. The increase in temperature of a 200°C resulted in a significant reduction in corrosion resistance, but it is still higher than the corrosion of the matrix material.

Practical implications: The aluminium alloy matrix composites reinforced with sintered preforms made by sintering halloysite nanotubes are modern materials that could find application in the automotive industry. The mechanical properties are greater than the alloy matrix while retaining a low density. It was necessary to examine the corrosion resistance as one of the important properties of the composites which are exposed to corrosive environments.

Originality/value: Beyond the articles of the authors, analysis of mechanical properties and corrosion resistance of the infiltrated AISi12 matrix composites reinforced by preform made by sintered halloysite were not found in the available literature.

Keywords: Corrosion behaviour; Infiltrated AISi12 matrix composite; Halloysite nanotubes

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PROPERTIES

1. Introduction

Metal matrix composites (MMCs) are one of the promising materials enjoying a lot of interest from industry, in particular, the automotive industry. Among them, especially desirable are composites with a light metal matrix, reinforced with ceramic particles or fibres. Thanks to the ceramic reinforcement obtain expected properties as compared with conventional alloys, such as lower density, increased strength, increased creep resistance, higher wear and corrosion resistance. An example of this type of material is cast aluminium alloy matrix reinforced with ceramic particles such as Al_2O_3 [1], SiC [2], B_4C [3] and TiC [4] or preforms based on Al_2O_3 [5].

An interesting challenge is the use of a reinforcement in the form of ceramic preforms on the base on halloysite nanotubes in aluminium alloy matrix composites [6]. The use of such reinforcement increases the hardness, bending strength, resistance to wear, and reducing thermal expansion as compared to the alloy matrix [7].

In addition to these properties in the case of aluminium alloy composites, it is necessary to get a good corrosion resistance. Aluminium is known for its high resistance to corrosion, by automatically overlapping passive protective oxide film Al_2O_3 , which prevents further oxidation. A comparable phenomenon occurs in the case of aluminium alloys. Their chemical composition may contain alloying elements favourable corrosion resistance as Cu, Mn, Si, Mg and Zn. They may also be those whose task is to create intermetallic phases designed to improve the mechanical properties. The presence of these phases in the structure can lead to a decrease in local corrosion resistance of alloy, which is related to the differences in electrochemical potentials, especially electrode potentials of the matrix and precipitate [8]. In the same way, particles or fibres of ceramic phase introduced to the alloy can affect the corrosion.

Introduction of the alloy of the ceramic phase can result in reduced resistance to corrosion, by factors such as [9, 10]:

- porosity at the matrix/reinforcement interface,
- chemical and phase composition of the interface (e.g. segregation of alloying elements),
- intermetallic precipitations,
- high dislocation density and tensile residual stresses around reinforcing phase,
- creating a galvanic cell between an active aluminium matrix composite material and more noble material gain.

Reinforcement may contribute to changes in the propagation of corrosion changes in composites due to electrochemical and chemical interactions between the matrix and reinforcement, the type of structure and the

problems associated with their processing. It not without significance is also the morphology and mass fraction of reinforcement. Quite often composites have a lower corrosion resistance as compared to the alloy matrix [11-16].

The paper presents the results of susceptibility to corrosion infiltrated composites with the AlSi12 alloy matrix, reinforced with preform made by sintered halloysite nanotubes. The aim of this work was to determine the effect of reinforcement content and temperature of sintering on the corrosion behaviour of the infiltrated composite material with aluminium alloy matrix in a corrosive environment, concerning the matrix alloy.

2. Materials and methodology

2.1. Material and technology

The material for the study were composite materials made by gas pressure infiltration (GPI) of porous, ceramic preforms base on halloysite nanotubes (Fig. 1a) by liquid AlSi12 aluminium alloy.

In the first step of fabrication of porous ceramic preforms was prepared using:

- Mechanical dry milling of a mixture of halloysite nanotubes (delivered by NaturalNano) with 30, 40 and 50wt.% addition of open pore forming agent in the form of carbon fibres Sigrafil CIO M250 UNS (SGL Carbon Group) (Fig. 1b) and 1% addition of lubricant MA7050, in a centrifugal ball mill Fritsch Pulverisette 6 for 15 minutes at 400 rpm.

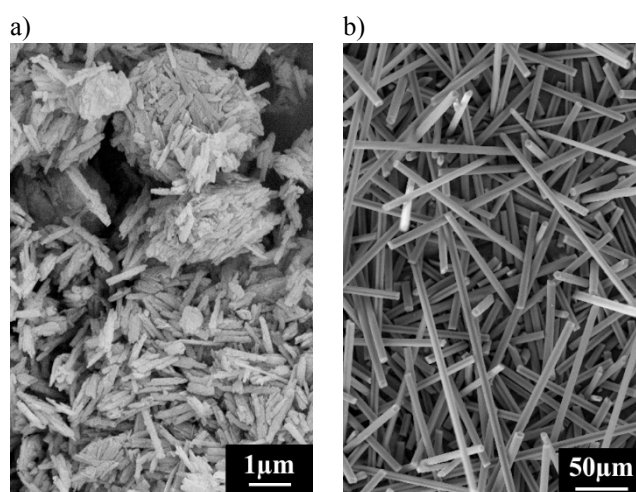


Fig. 1. Morphology of as-received a) halloysite nanotubes and b) carbon fibres

- Compacting the resulting mixture by uniaxial pressing (cold) in a rectangular matrix of 12×35 mm in plate hydraulic press Fontijne LabEcon 600 Grotnes. Samples were compacted at a pressure of 50, 75 and 100MPa for 15 seconds.
- Sintering the green compacts in a high temperature furnace PRS 75W in an atmosphere of air (5 l/h), consisting of treatments such as a slow heating to a temperature of degradation of carbon fibres; annealing at a temperature of 800°C (favouring the degradation of the carbon fibres in the entire volume of the sample); additional heating to the sintering temperature; sintering (1300 and 1500°C) and free cooling (Fig. 2).

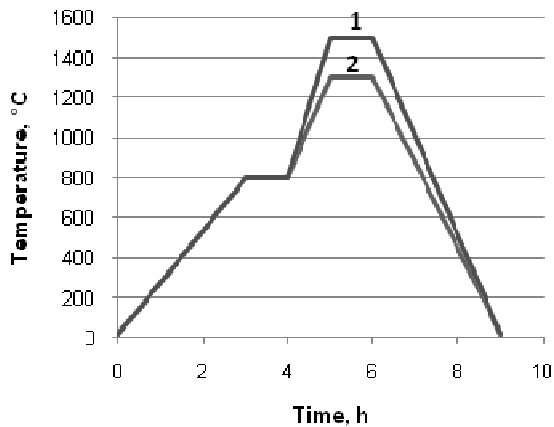


Fig. 2. Diagram of the sintering process

In the end of sintering process ceramic preforms with open porosity were obtained. Fractographic analysis made by the use of scanning electron microscopy revealed that preforms have open pores with a uniform distribution (Fig. 3a). Higher magnification showed a needle-like microstructure defined as *mullite whiskers* (Fig 3b).

Metal matrix composites (Fig. 4b) were obtained by gas pressure infiltration of porous ceramic preforms by AlSi12 aluminium alloy (EN-AB 44200 PN-EN 1706) in the crucible furnace with a gas-tight autoclave pressure infiltration of porous structures PTA-8/PrGC. The chemical composition of the alloy is shown in Table 1.

Table 1. Chemical composition of AlSi12 aluminium alloy

Mass fraction of the element, wt.%							
Al	Si	Fe	Zn	Mn	Cu	Mg	Ti
Bal.	10.85	0.35	0.04	0.004	0.003	0.001	0.00

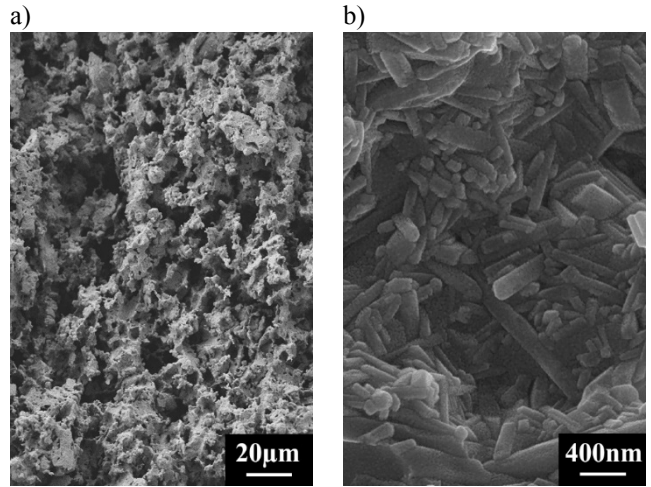


Fig. 3. Fracture topography of the porous ceramic preforms fabricated with an addition of 50 wt% carbonfibres (a) and morphology of mullite whiskers (b), SEM

The isostatic gas pressure infiltration was carried out in a nitrogen atmosphere at a pressure of 3 MPa at 800 °C and time of 30 seconds. As a result, obtained composite materials characterised by interpenetrating phases of metal and ceramics (Fig. 5).

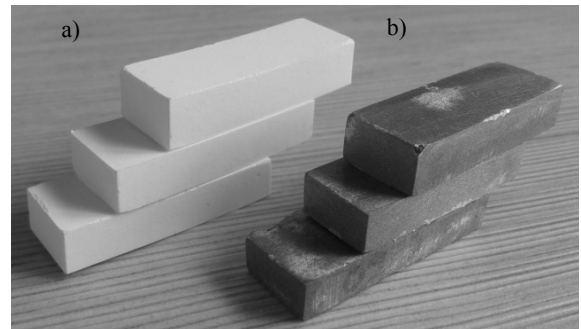


Fig. 4. Samples of porous ceramic preforms (a) and infiltrated metal matrix composites (b)

The obtained composites reinforced by ceramic preforms are characterised by a uniform distribution of reinforcing phase and the almost complete filled pores by liquid aluminium alloy. In the phase composition of composites reinforced with ceramic preforms, it can be seen a number precipitations of coarse silicon which tend to crystallise on the surface of the ceramic phase (Fig. 6). Fabricated metal matrix composites is characterised by the microstructure of α -Al with $\alpha+\beta$ eutectic constituting the matrix and coarse grains of β . Mullite as a reinforcing phase has been also identified (Fig. 6).

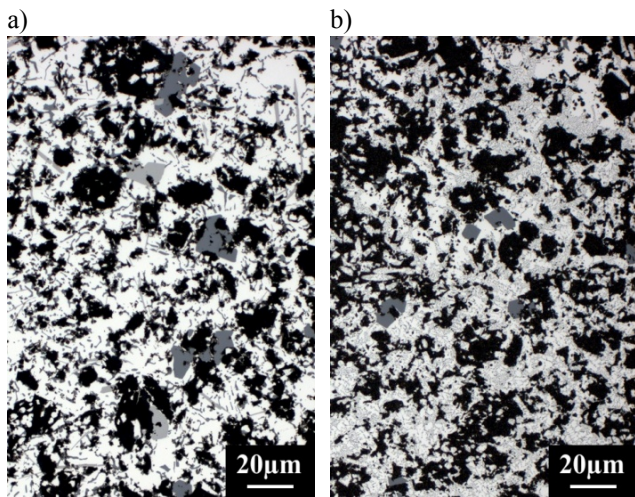


Fig. 5. The structure of non-etched metal matrix composite materials with 50wt.% HNTs sintered at a) 1300°C and b) 1500°C

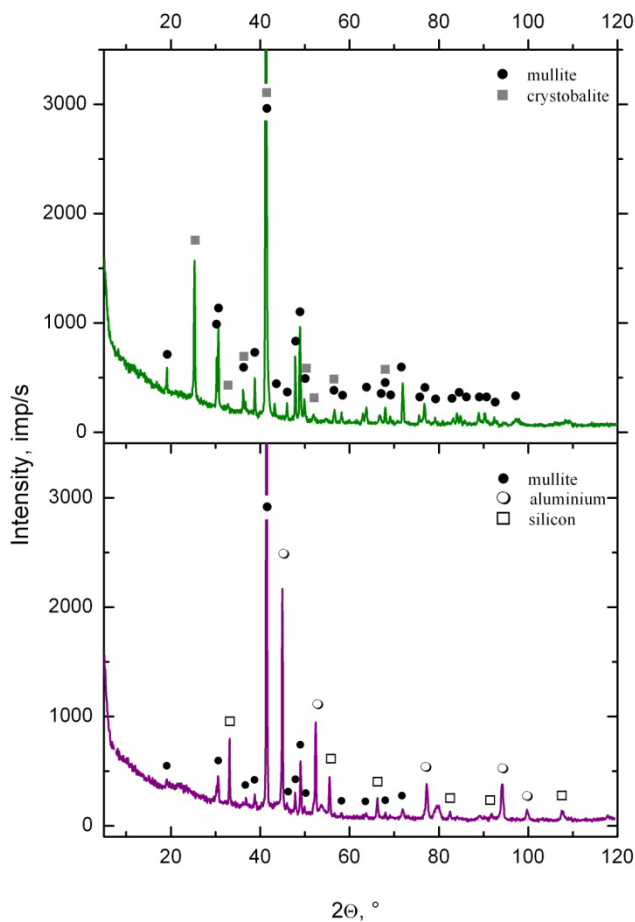


Fig. 6. The X-ray phase analysis results of a) sintered porous preforms and b) infiltrated composite materials

2.2. Research methodology

The corrosion resistance research was made with a potentiodynamic method on the Potentiostat-Galvanostat ATLAS 0531 according to PN-EN ISO 17475:2010 standard. Test samples were grinded on SiC papers 500, 800 and 1200 $\mu\text{m}/\text{mm}^2$ grain size and afterwards, there were cleaned in acetone. The surface area of tested samples was 0.195 cm^2 . Electrochemical corrosion research was done in water centre of 3% NaCl at room temperature. In the research were used three electrodes: a working electrode (the sample), the reference electrode Ag/AgCl and steel auxiliary electrode (Fig. 7).

Electrochemical studies of corrosion resistance were performed in two stages. The first step determined open circuit potential E_{ocp} for one hour. The second stage relied on saving the anodic polarisation curves by applying to potential changes in the direction of anode and cathode at 1 mV/s. The initial value was determined based on $E_{\text{ocp}} - 100$ mV. When the potential reaches a value of 500 mV or current density was 1 mA/cm^2 direction of polarisation was reversed and potential back to start point.

Based on the registered anodic polarisation curves the characteristic values of pitting corrosion were determined: corrosion potential (E_{kor}), passive layer breakdown potential (E_{cp}), corrosion current density (i_{cor}), polarisation resistance (R_p). The value of corrosion current was determined using the Tafel extrapolation.

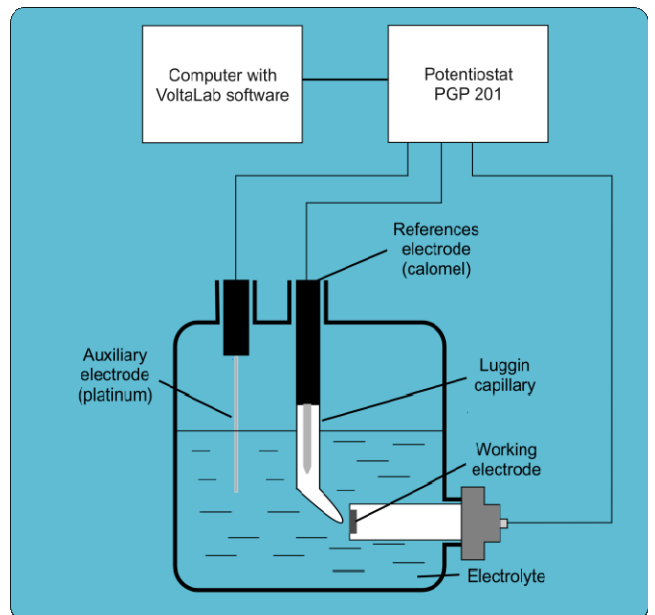


Fig. 7. Diagram of the potentiostat used in corrosion test

3. Results and discussion

The first stage of the corrosion tests was determined the free potential in non-current conditions. For all the specimens open circuit potential was almost the same and it ranged from -697 to -668 mV and because the potential difference was less than 5% those results were not a criterion for assessing the impact of carbon nanotubes composition on the corrosion resistance of manufactured composite materials. The second stage results of the corrosion resistance test were presented, as two curves correspond to $j=f(E)$ and $\log(|j|)=f(E)$ where j is anodic current density and E is a potential (Fig. 8).

On the basis of recorded anodic polarization curves in the anode and cathode direction using the Tafel extrapolation method was calculated corrosion potential (E_{cor}) and current density (i_{cor}). Additionally, in place of the breakdown of the passive layer formed during polarization of the samples was determined pitting initiation potential (E_b) all results were showed in Figure 9 and in Table 2.

Similar as in the case of comparing the free potential, comparing the corrosion and breakdown potential of composite materials there was no significant impact on the carbon nanotubes composition on anti-corrosion properties.

The corrosion potential was changed from -690 to -634 mV, the difference between the smallest and largest value was approximately 8%. Whereas the breakdown potential was changed from -617 mV for casting samples to -559 mV for samples after sintered in 1500°C, the difference between the extreme values was approximately 9%.

When comparing corrosion current density determined by the Tafel method and polarization resistance of tested materials, there is a possibility to confirmed the relationship between then-the higher current value a lower value of resistance polarization and vice versa. Based on the results were found that the proportion of nanotubes in tested composite materials does not change the corrosion resistance, characteristic electrochemical values did not change, while there was significantly influenced by when compare results from different sintering temperature (Fig. 10). Increasing the sintering temperature from 1300 to 1500°C increased the corrosion current from around 0.5-0.8 $\mu\text{A}/\text{cm}^2$ to approximately 4.3 $\mu\text{A}/\text{cm}^2$.

According to that relationship the corrosion current changes affected on the polarization resistance of test materials because increasing the sintering temperature from 1300 to 1500°C resulted in the reduction the resistance from 20 to 30 $\text{k}\Omega\cdot\text{cm}^2$ to about 3.5 $\text{k}\Omega\cdot\text{cm}^2$. Referring the results of corrosion of the AlSi12 matrix material into the manufactured composite was found that the alloy after casting characterized a lower corrosion resistance as evidenced by the corrosion current and the resistance of these samples.

The corrosion current for the matrix material was higher than the samples sintered at 1500°C more than 50%, and in comparison to the samples after sintering at 1300°C higher by one order of magnitude. When comparing the value of resistance studied materials the matrix alloy characterized by a resistance lower by more than half compared to the sintered obtained at a temperature 1500°C and about 15 times lower compared to the samples after sintering at 1300°C.

Table 2.
Electrochemical corrosion parameters of tested composite materials

	x_c50*	x_c60*	x_c70*	z_c50*	z_c60*	z_c70*	cast (AlSi12)	
E_{ocp}	-697	-683	-682	-680	-668	-680	-690	mV
R_p	31	20	26	3.6	3.7	3.3	1.7	$\text{k}\Omega\cdot\text{cm}^2$
E_{cor}	-690	-643	-652	-664	-655	-634	-664	mV
i_{cor}	0.510	0.584	0.858	4.3	4.4	4.2	6.7	$\mu\text{A}/\text{cm}^2$
E_b	-596	-562	-577	-590	-559	-590	-617	mV

* pressure of compacting: c - 100 MPa; sintering temperature of preforms: z - 1500°C, x - 1300°C; mass fraction of halloysite nanotubes: 50, 60, 70%

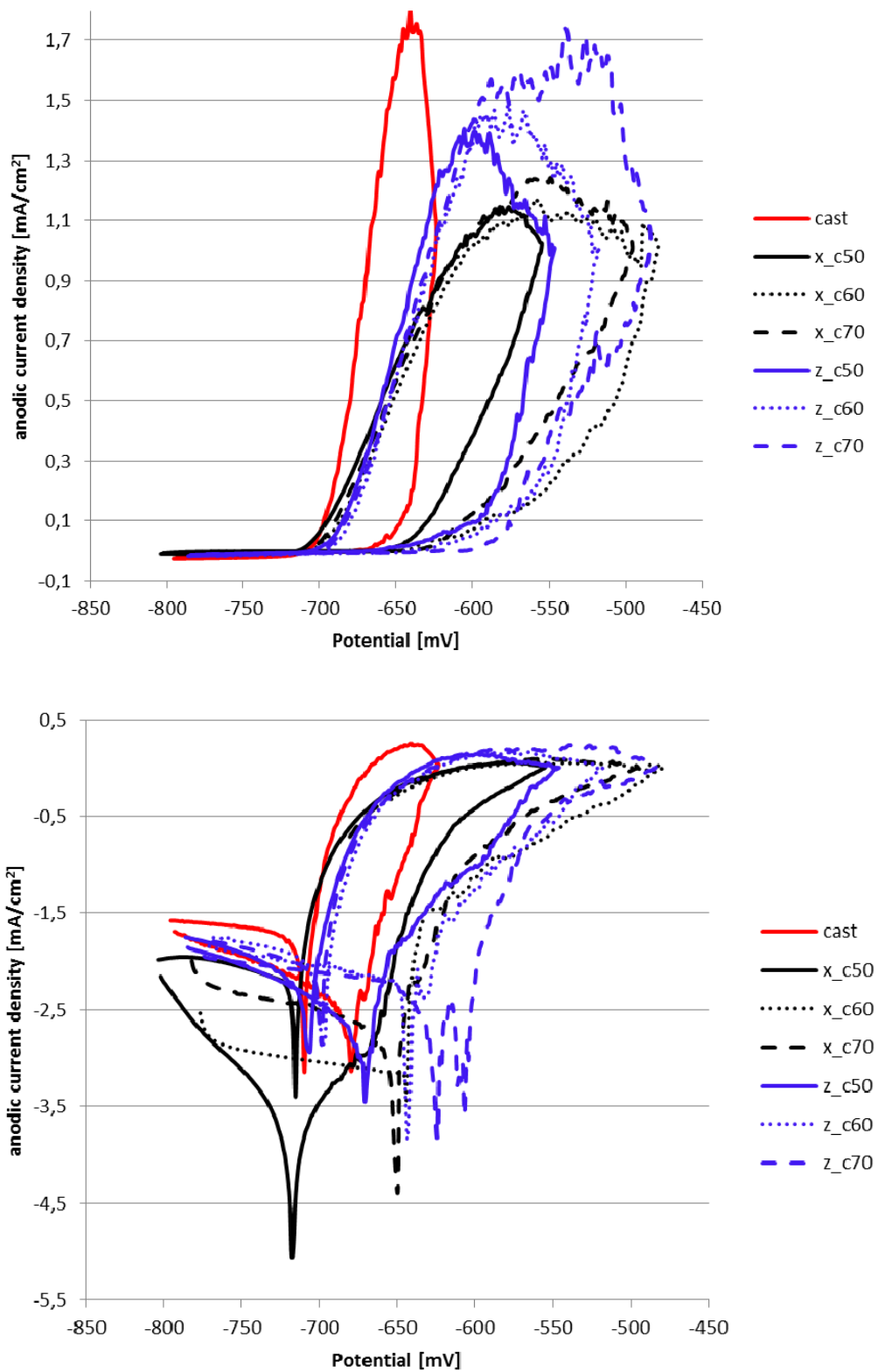


Fig. 8. Electrochemical characterization recorded in the study of corrosion resistance

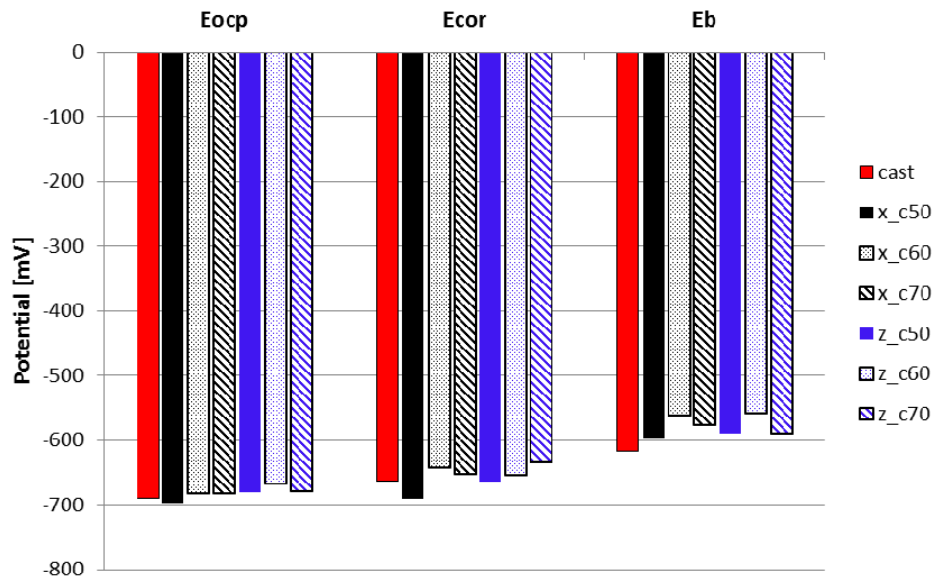


Fig. 9. Typical values of potential for tested composite materials determined during the corrosion research

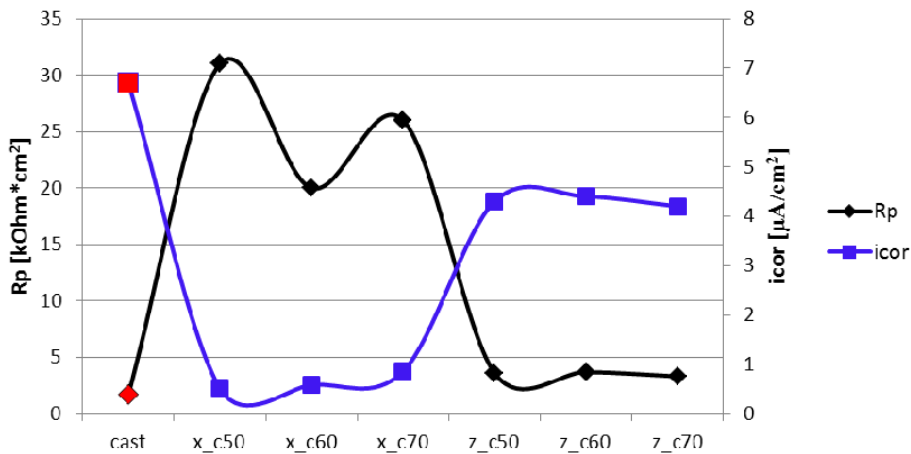


Fig. 10. Influence of nanotubes proportion and sintering temperature on the corrosion resistance of tested composite materials

4. Conclusions

In the research work, the corrosion behaviour of infiltrated composite materials reinforced with ceramic preforms in NaCl was investigated. Metallographic investigations of infiltrated composite materials has shown the percolation type of the microstructure, a homogeneous distribution of the mullite phase and the absence of unfilled pores.

The results indicate that change the concentration of halloysite nanotubes between 50 and 70% in the

manufactured composite materials did not effect on their corrosion resistance. Increasing the sintering temperature of studied materials from 1300 to 1500°C was related to increasing the corrosion current 7-times and decrease in resistance 9-times, what indicates a reduction in corrosion resistance of sintered materials at higher temperatures. Fabricated composite materials are characterized by improved resistance to corrosion than AlSi12 alloy used as the matrix. The main reason is that a corrosion current value of the alloy is higher by more than one order of magnitude compared to composite materials, and the value of polarization resistance was even one order of magnitude lower.

Acknowledgements

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