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CORROSION STUDIES ON ALUMINIUM-BASED METAL MATRIX COMPOSITES REINFORCED WITH GRAPHITE, SiC AND FLY ASH PARTICLES

Aluminium Matrix Composites reinforced with ceramic particles (e.g. SiC, Al₂O₃, graphite and fly ash) are actually advanced engineering materials. These materials can be characterised by superior mechanical and thermal properties. However, the addition of the reinforcement particles could significantly changing corrosion behaviour of aluminium matrix composites. The corrosion resistance of aluminium matrix composites is determined by several factors such as: variety of aluminium alloy matrix and reinforcement type combinations, manufacturing technology, microstructure of composite and interfacial reactions reinforcement/matrix. This paper presents microstructural characteristic and susceptibility to pitting corrosion of on aluminium-based metal matrix (Al-Si) composites reinforced with graphite (5.7 wt. %), SiC (20 vol. %) and fly ash (9.0 wt. %) particles. The corrosion resistance experiments were carried out by accelerated electrochemical studies using the potentiodynamic method (in the 3.5 wt. % NaCl aqueous solution, pH 7.0, at 25°C). The corrosion behaviour of composite with fly ash particles was studied further by immersion tests for 50 days (3.5 wt. % NaCl). The polarisation curves, corrosion potentials (corrosion E_{corr} , pitting E_{pit} and repassivation E_{rp}) and surface morphology after corrosion tests were estimated. It was found that: (1) the electrochemical data and microstructure observations after corrosion tests confirms that incorporation of reinforcement particles (graphite, SiC, fly ash) into aluminium matrix causes the increase of susceptibility to pitting corrosion of the composites in comparison with unreinforced matrix alloys, (2) the enhanced pitting corrosion of Al/fly ash, Al/SiC and Al/GR composites is associated with the pores, multiphasic character of composites (e.g. the releases of intermetallic Al₃Ni phase), reactions at the interface reinforcement/matrix and formation of galvanic couples favourable to corrosion. The same factors also determine the properties of oxide film forming on the materials surface.

Keywords: aluminium, metal matrix composites, microstructure, pitting corrosion

BADANIA ODPORNOŚCI KOROZYJNEJ MATERIAŁÓW KOMPOZYTOWYCH O OSNOWIE ALUMINIUM ZBROJONYCH CZĄSTECZKAMI GRAFITU, SiC I POPIOŁU LOTNEGO

Materiały kompozytowe o osnowie aluminium zbrojone cząsteczkami ceramicznymi (np. SiC, Al₂O₃, grafit i popiół lotny) stanowią aktualnie nowoczesne materiały inżynierskie. Materiały te charakteryzują się wysokimi właściwościami mechanicznymi i termicznymi. Jednakże wprowadzenie cząsteczek zbrojących do osnowy może znacząco zmieniać zachowanie korozyjne kompozytów. Odporność korozyjna kompozytów o osnowie aluminium uwarunkowana jest kilkoma czynnikami, takimi jak: różnorodnością materiałów osnowy oraz faz zbrojących, technologią wytwarzania, mikrostrukturą kompozytów oraz reakcjami na powierzchni rozdziału osnowa/zbrojenie. W artykule przedstawiono charakterystykę mikrostrukturalną i podatność do korozji wżerowej kompozytów o osnowie stopów aluminium (Al-Si) zbrojonych cząsteczkami grafitu (5,7% wag.), SiC (20% obj.) oraz fly ash'u (9% wag.). Odporność korozyjną określono za pomocą przyspieszonych badań elektrochemicznych metodą potencjodynamiczną (3,5% wag. NaCl, pH 7,0, 25°C) oraz dodatkowo dla kompozytu zbrojonego cząsteczkami fly ash'u badaniami zanurzeniowymi (przez 50 dni w 3,5% wag. NaCl). Wyznaczono krzywe polaryzacji, typowe potencjały korozyjne (korozji E_{corr} , przebicia E_{pit} i repasywacji E_{rp}) oraz analizowano morfologię powierzchni po przeprowadzonych badaniach korozyjnych. Wykazano, że: (1) dane elektrochemiczne oraz obserwacje mikrostruktury po przeprowadzonych badaniach korozyjnych potwierdzają, że wprowadzenie cząsteczek zbrojących do osnowy aluminiowej powoduje wzrost podatności do korozji wżerowej materiałów kompozytowych w stosunku do stopów osnowy, (2) korozja wżerowa kompozytów Al/fly ash, Al/SiC i Al/GR związana jest z porowatością, wielofazowym charakterem kompozytów (np. wydzielenia fazy Al₃Ni), reakcjami na powierzchni rozdziału osnowa/zbrojenie oraz tworzeniem się par galwanicznych sprzyjających korozji. Czynniki te determinują także właściwości warstwy pasywnej na powierzchni materiałów.

Słowa kluczowe: aluminium, metalowe materiały kompozytowe, mikrostruktura, korozja wżerowa

INTRODUCTION

Aluminium Matrix Composites (AMCs) reinforced with ceramic particles are actually advanced engineering materials. The most common reinforcement materials in discontinuously reinforced aluminium compos-

ites are SiC, Al₂O₃, graphite and other, for example fly ash. The AMCs can be characterised by superior mechanical (higher strength to weight ratio, stiffness, modulus and wear resistance) and thermal or electrical

properties [1]. The composites are usually manufactured by the most inexpensive and flexible casting methods (stir casting, squeeze casting). AMCs can be used in aerospace and automotive industries as parts of driving mechanisms and engines, undercarriage, steering systems, bodies and parts of the braking systems, air-frame components [2].

However, the addition of the reinforcement particles could significantly changing corrosion behaviour of aluminium matrix composites. Composite materials can have lower resistance to corrosion than aluminium alloys compared to their base metals. The corrosion behaviour of AMCs is determined by several factors such as: variety of aluminium alloy matrix and reinforcement type combinations, manufacturing technology, microstructure of composite and interfacial reactions reinforcement/matrix [3-7].

The paper presents results of the studies on the susceptibility of aluminium matrix composites to corrosion. The aim of the investigation was estimate the influence of ceramic particles and microstructure of composites to pitting corrosion, in typical corrosive environment.

EXPERIMENTAL PROCEDURE

The subject of the examination were composites:

- Al/GR – matrix: AlSi alloy (11.3÷13% Si, 0.8÷1.3% Cu, 0.8÷1.5% Mg, 0.8÷1.1% Ni; wt. %); reinforcement: 5.7 wt. % of graphite particles coated with Ni (60 wt. %) of average diameter 75÷120 μm ,
- Al/SiC – matrix: AlSi alloy (8.5÷9% Si, 0.45÷0.65% Mg, 0.2% Cu; wt. %); reinforcement: 20 vol. % of silicon carbide particles of average diameter 20 μm ,
- ALFA – matrix: AlSi alloy (11.3÷13% Si, 0.8÷1.3% Cu, 0.8÷1.5% Mg, 0.8÷1.1% Ni; wt. %); reinforcement: 9.0 wt. % of fly ash particles of average diameter 75-120 μm .

The composites has been synthesized at the Foundry Research Institute in Cracow (gravity casting - vortex method).

The corrosion resistance experiments were carried out by accelerated electrochemical studies using the potentiodynamic method. The potentiodynamic measurements were made in the 3.5 wt. % NaCl aqueous solution of pH 7.0 at 25°C, with Pt counter-electrode. Polarization was started at a potential of -1900 mV shifting the potential towards the anodic side till a clear increase in the current density and the measurements were recorded again on the cathodic side (shift at a rate of 10^{-3} V). The potential was controlled with an EG-20 type generator, EP-20 potentiostat and a PC equipped with reference to a saturated calomel electrode. The polarisation curves and corrosion potentials (corrosion E_{corr} , pitting E_{pit} and repassivation E_{rp}) were determined.

The corrosion behaviour of ALFA composite was studied further by immersion tests for 50 days (3.5 wt. % NaCl). Every 5 days the specimen were first mechanically and chemically cleaned with a brush made of plastic strings, and then chemically cleaned, dried and weighed.

The microstructure and the surface morphology analysis of materials were performed by X-ray diffraction technique (HZG-4), optical microscope (ZEISS model) and scanning electron microscopes (LEO 1430VP with EDX-Roentec).

RESULTS AND DISCUSSION

The typical microstructures of composites are presented in Figure 1.

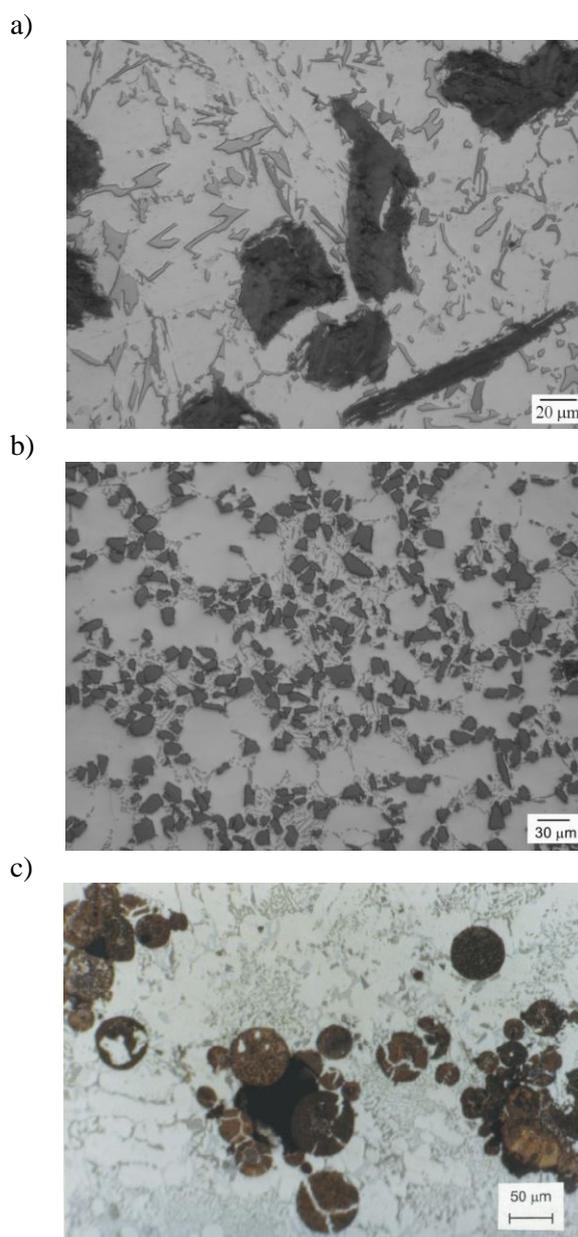


Fig. 1. Microstructure of composites: a) Al/GR, b) Al/SiC, c) ALFA
Rys. 1. Mikrostruktura materiałów kompozytowych: a) Al/GR, b) Al/SiC, c) ALFA

Quite uniform distribution and good bonding between ceramic particles and the matrix alloys were noted. However, in the case of ALFA composite agglomerations of fly ash particles and porosity were observed. The porosity was located in the neighbourhood of interface reinforcement/matrix. The X-ray analysis of Al/GR composites confirms the occurrence of Al₃Ni intermetallic phase. Any visible Al₄C₃ phase, often indicated in AMCs, has been found in the microstructure (Fig. 2).

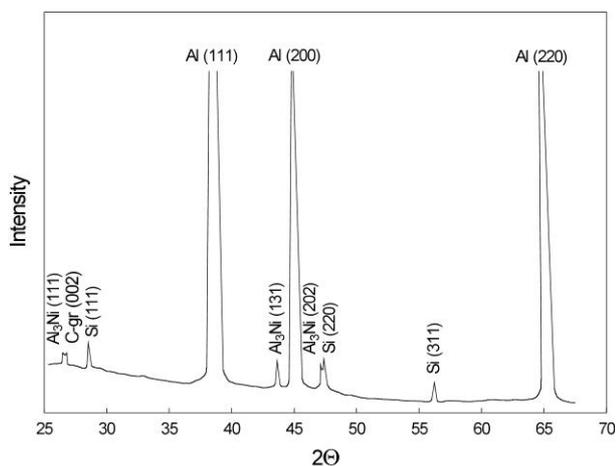


Fig. 2. X-ray diffraction pattern of Al/GR composite (CuK_α X-ray, 35 kV/30 mA)

Rys. 2. Dyfraktogram kompozytu Al/GR (CuK_α, 35 kV/30 mA)

The representative polarisation curves of the investigated materials in 3.5 wt. % NaCl aqueous solution are presented in Figure 3, while the values of the potentials E_{corr} , E_{pit} , E_{tp} and depth of pits are listed in Table 1.

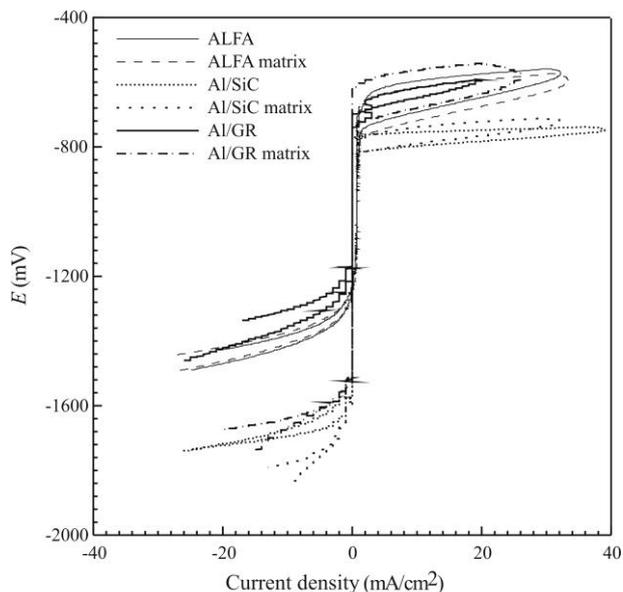


Fig. 3. The representative potentiodynamic polarization curves of composites and matrix alloys

Rys. 3. Reprezentatywne krzywe polaryzacji potencjodynamicznej kompozytów i stopów osnowy

Electrochemical potentials (such as E_{corr} , E_{pit} , E_{tp}) of ALFA and Al/GR composites are lower than that of unreinforced matrix alloys. In the case of Al/SiC composites similar electrochemical data for both matrix and composite is noted. More positive values of main electrochemical potentials indicate slightly higher corrosion resistance of matrix alloys in comparison with composites.

TABLE 1. Electrochemical data and depth of pits of materials from the corrosion testing

TABELA 1. Dane elektrochemiczne i głębokość wżerów wyznaczone podczas testów korozyjnych

Materials	E_{corr} mV	E_{pit} mV	E_{tp} mV	Depth of pits μm
ALFA matrix	-735	-613	-739	6÷40
ALFA	-763	-640	-764	8÷50
Al/SiC matrix	-830	-787	-831	8÷16
Al/SiC	-820	-767	-827	10-24
Al/GR matrix	-722	-583	-721	8÷14
Al/GR	-750	-648	-688	20÷44

Figure 4 presents typical microstructure of the surfaces of samples after corrosion study. In these cases crystallographic etching may be observed. The initiation of corrosion pits takes place in α +Si eutectic (for matrix alloys), while in the case of composites numerous corrosion pits were observed which occur in the solid solution α -Al. The pits also locate nearby ceramic particles. The degradation of interface reinforcement/matrix alloy around particles was observed. The depth of corrosion pits for examined composites is higher than in matrix alloys.

The results of the weight loss experiments as a function of corrosion time are shown in Figure 5. It may be seen from the figure that in the case of ALFA composite the weight loss regularly increases with time in the entire range of time up to 50 days. However, in the case of matrix alloy the weight loss attains a constant value after about 25 days.

Therefore, the difference in their corrosion behaviour may be attributed to the difference in the formation of oxide films (the oxide film formed on the matrix alloy surface is compact, adherent and pore-free).

Generally, presence of reinforcing phase is the main factor causing higher susceptibility to corrosion of composites, due to of changes in composites structure, particularly the weakening of passive layer [5, 7, 8]. The introduction of reinforcing materials, such as graphite, SiC and fly ash particles to the active aluminium matrix alloy and the reaction products between reinforcement and matrix lead to the formation of galvanic couples causing corrosion [6, 8].

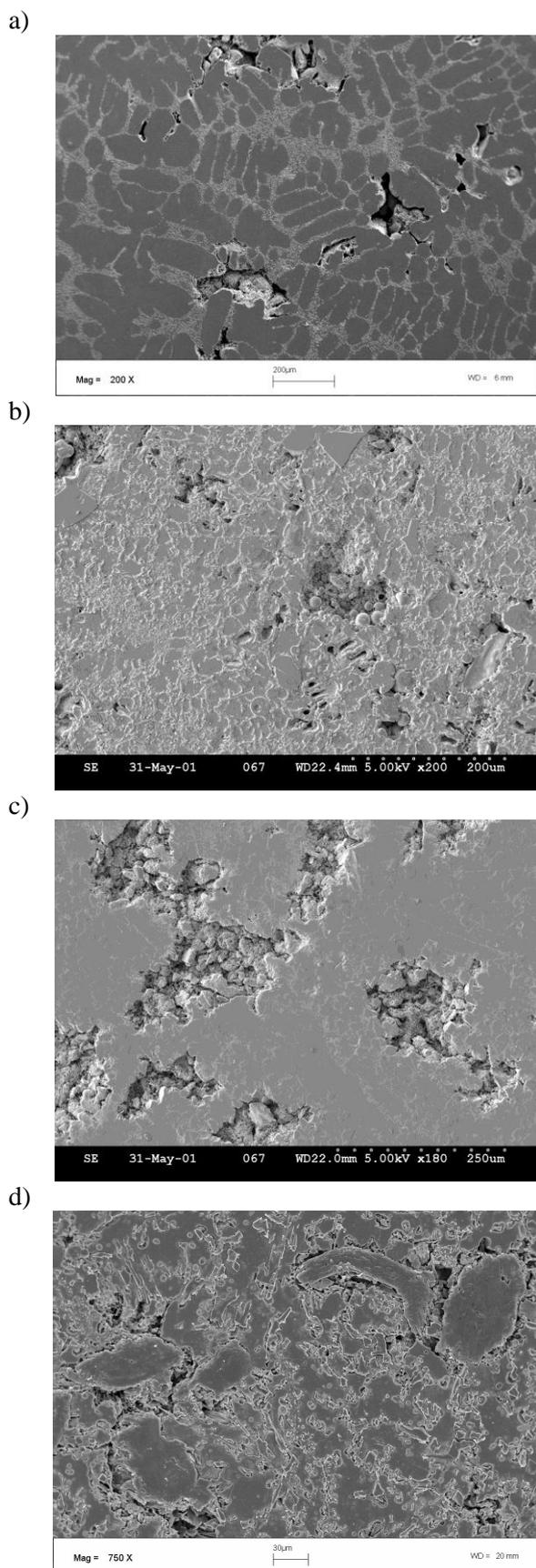


Fig. 4. SEM microphotograph of pitting corrosion on the surfaces of: a) matrix alloy, b) ALFA, c) Al/SiC, d) Al/GR

Rys. 4. Korozja wżerowa na powierzchni: a) stopu osnowy, b) ALFA, c) Al/SiC, d) Al/GR

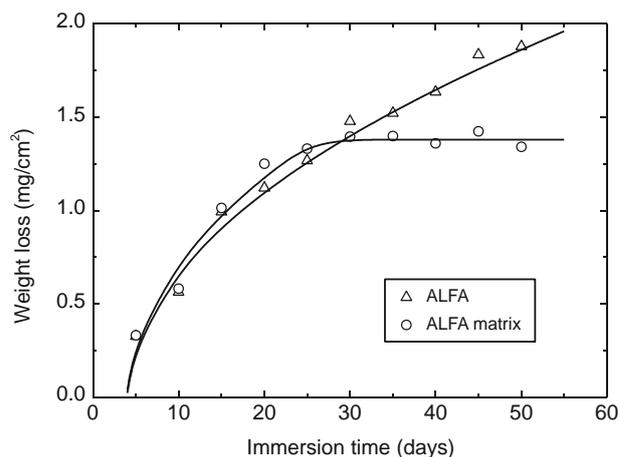


Fig. 5. Weight loss of ALFA composite and matrix alloy after immersion test for 50 days in 3.5 wt. % NaCl aqueous solution

Rys. 5. Ubytek masy kompozytu ALFA i stopu osnowy po badaniach zanurzeniowych w roztworze 3,5% NaCl

Pitting corrosion appears mainly on metals and alloys in the passive state as a result of disarrangement of passive layer by aggressive environment elements (frequently Cl^- ions) on the heterogeneities of metals. Pit initiation involves the adsorption of Cl^- at the flaws in the surface oxide films (for example: casting defects, second-phase particles), followed by chemical reaction between the Cl^- and the oxide [9]. In the case of composites introduction of considerable amounts of alloy additions and reinforcing materials to the aluminium matrix releases intermetallic phases in the structure. Moreover, factors influencing corrosion of the composites include porosity, segregation of alloying elements to the reinforcement/matrix interface, presence of an interfacial reaction product, high dislocation density around the reinforcement phase, microporosity and voids at the reinforcement/matrix interface and electrical conductivity of the reinforcements [10-13].

The initiation of pits are indubitably connected with the quality of passive layer on the surface of composites [6, 14]. It's a well-known fact, that corrosion resistance is higher along with the increase of surface homogeneity of materials. Therefore, higher corrosion of aluminium-based composite may appear in this study. Moreover, the release of intermetallic phase in the composites structure e.g. Al_3Ni , which consequently form „cathode patches” with good conductive properties of the passive layer [12]. The intermetallic Al_3Ni phase is formed in the process of fabrication of Al/GR composite due to reaction between liquid metal matrix and graphite particles covered with nickel. It can be suggested that Ni plays double role in Al/GR composites. Firstly it stimulates physical-chemical interaction between liquid matrix alloy and reinforcing phase and secondly can protect graphite particles against over interaction with molten metal [4]. The presence of a more conductive phase at

the interface provides an easier path for the electron exchange necessary for oxygen reduction and drives the anodic reaction at a higher rate in the AMCs as compared to an aluminium alloy [8]. The formation of corrosion pits can be divided into of two stages [4]. First state is the reaction between secondary phases and consequently the dissolution of metal and break-down of passive layer were observed. In the next stage, changes in pits plays the main role in development of corrosion process.

From the point of view of corrosion behaviour porosity observed in the composites microstructure is also important. During the corrosion process an increase in the concentration of aggressive Cl^- anions and H^+ ions may occur in the pits and pores due to impeded replenishment of the solution. Due to the increase in the concentration of Cl^- and H^+ ions passivation becomes difficult. Therefore, dissolution of metal in the pits is stimulated [9].

Pitting in composites has often been observed at the reinforcement-matrix interfaces [8, 10]. It may be a result of the presence of an interfacial reaction products formed during composite production. The segregation of alloy addition, formation of Al_4C_3 and intermetallic releases at the interface, between matrix and reinforcing, were observed. It prevents the formation of passive layer on the entire surface. In composites reinforced with particles, the presence of Al_4C_3 and other hydrophilic compounds is unfavourable (Al_4C_3 reacts with water). The degradation of interface reinforcement/matrix occurs [11]. The conducted studies did not confirm the presence of Al_4C_3 in the microstructure of composites.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The electrochemical data and microstructure observations after corrosion tests confirms that incorporation of reinforcement particles (graphite, SiC, fly ash) into aluminium matrix causes the increase of susceptibility to pitting corrosion of the composites in comparison with unreinforced matrix alloys.
2. The enhanced pitting corrosion of ALFA, Al/SiC and Al/GR composites is associated with the pores, multiphasic character of composites (e.g. the releases of intermetallic Al_3Ni phase), reactions at the interface reinforcement/matrix and formation of galvanic couples favourable to corrosion. The same

factors also determine the properties of oxide film forming on the materials surface.

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