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Corrosion resistance of the sintered composite materials with the EN AW-AICu4Mg1(a) alloy matrix reinforced with ceramic particles

A. Włodarczyk-Fligier, M. Adamiak, L.A. Dobrzański*

Institute of Engineering Materials and Biomaterials,

Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland * Corresponding author: E-mail address: leszek.dobrzanski@polsl.pl

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Properties

<u>ABSTRACT</u>

Purpose: the aim of the project was to evaluate of the effect of heat treatment and the reinforcing Al_2O_3 and Ti(C,N) particles content on the corrosion resistance in the NaCl water solution environment on the EN AW-AlCu4Mg1(A) aluminium alloy matrix composite.

Design/methodology/approach: Powders of the starting materials were wet mixed in the laboratory vibratory ball mill to obtain the uniform distribution of the reinforcement particles in the matrix. The mixed powders were then dried in the air. The components were initially compacted at cold state in a die with the diameter of \emptyset 26 mm in the laboratory vertical unidirectional press – with a capacity of 350 kN. The selected compacting load was sufficient to obtain prepregs which would not crumble and at the same time would not be deformed too much, which would also have the adverse effect on their quality, as the excessive air pressure in the closed pores causes breaking the prepreg up when it is taken out from the die. The obtained PM compacts were heated to a temperature of 480-500°C and finally extruded – with the extrusion pressure of 500 kN. Someofthe compositematerials werehyperquenched for 0.5 hat the temperature of 495°C with the subsequent cooling in water, and were quench aged next for 6 h at 200°C. Corrosion tests were made in 5% water NaCl solution.

Findings: Composite materials were examined without heat treatment and after heat treatment carried out to improve their corrosion resistance. The corrosion susceptibility of the investigated composite materials determined using the potentiodynamic method in the 3% water solution of NaCl depends on the volume fraction of the reinforcing particles and also on the heat treatment status.

Practical implications: Tested composite materials can be applicate among the others in automotive industry but it requires additional researches.

Originality/value: It was demonstrated corrosion resistance of the extruded composite materials with the EN AW-Al Cu4Mg1(A) alloy matrix may be formed by the dispersion hardening with the Al_2O_3 and Ti(C,N) particles in various portions and by the precipitation hardening of the matrix.

Keywords: Aluminum alloy; Composite materials; Corrosion resistance

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1. Introduction

For many years composite materials have been widened their share on the engineer materials market and what is even more important a demand for them is constantly increasing in quantitatively and qualitative way. Thanks to researches all over the world, the technological difficulties, associated with manufacturing processes, are overcame, particularly for the composite with metal matrix. More over the spectrum of the design rules and the properties improvement of these material group have been bounded [1].

Composites with an aluminium alloy matrix (AIMMC) are a group of materials which due to their properties (high specific elasticity modulus, high stiffness) are more and more frequently used in modern engineering constructions. Composites reinforced with ceramic particles (Al₂O₃, SiC, Ti(C,N), BN) are gradually being implemented into production in automotive, electronic or aircraft industries, first and foremost due to high resistance to friction wear [2-6].

Employment of the hard particles as reinforcement increases their hardness, Young's modulus and abrasion wear resistance, corrosion resistance; however, at also results in deterioration of their plastic properties. Heat treatment is carried out consisting in hyperquenching and ageing to improve their mechanical properties. Composite materials precipitation hardening occurs due to hyperquenching and ageing as a result of precipitation of the hard dispersive particles of the intermetallic phases. The intermetallic phases occurring in the aluminium alloys matrix most often are: Al₂Cu, Al₂CuMg, Al₂Mg, Al₃Mg, Cu₉Al₄, and Al₂Cu₃ [3-16].

Aluminium and its alloys are characteristic of high corrosion resistance in the standard atmospheric conditions and in the environment of many acids, thanks to the Al_2O_3 aluminium oxide layer developing on their surface [7,8,11,12]. Therefore, the corrosion resistance of aluminium depends on the solubility of its protective layer. Its tightness and good adhesion to the substrate, determining the corrosion resistance, is dependent on purity of aluminium or its alloys [8,13].

There are few literature sources on the influence of the ceramic particles on the pitting corrosion resistance of the composite materials with the aluminium matrix, and those available are often contradictory. On one hand it is said that the ceramic particles cause deterioration of the susceptibility of composite materials to corrosion due to the interfacial reactions, residual stresses, and the high density of dislocations around the particles; however, on the other hand investigations of the composite materials with the aluminium matrix reinforced with Al₂O₃ have proven the possibility of occurring the selective corrosion on the boundary of the ceramic and matrix material phases [11,13]. It has been presented in literature [7] that the Al₂O₃ ceramic particles with the sizes of 30 and 50 μ m cause the decrease of the corrosion resistance of the investigated materials.

These materials should exhibit good corrosion resistance in the aggressive environment therefore determining of the corrosion resistance of composite materials with aluminium matrix reinforced with ceramic additives is very important [6,9,10,17-19].

The goal of the project was evaluation of the effect of heat treatment and of the reinforcing Al_2O_3 and Ti(C,N) particles in the EN AW-AlCu4Mg1(A) aluminium alloy on the corrosion resistance in the NaCl water solution environment.

2. Experimental procedure

The investigations were made of the composite materials obtained with the powder metallurgy methods and by hot extrusion of the EN AW-AlCu4Mg1(A) aluminium alloy (Table 1) reinforced with the Al₂O₃ and Ti(C,N) phases particles with the mass portions of 5, 10, and 15%. The initial size of the matrix material powder particles is smaller than 75 μ m, of the reinforcement Al₂O₃ powder is smaller than 0.5 μ m, and of the Ti(C,N) powder is smaller than 25 μ m (Fig. 1, Table 2).

Table 1.

Chemical composition of EN AW-AlCu4Mg1(A) aluminium alloy,% vol.[20]

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others	Al
0.24	0.1	1.2- 1.5	0.1- 0.3	1.9- 2.9	0.04	0.10	0.09	0.20	The others

Table 2.

Particles size of powders used to investigated composites production

Powder type	EN AW- AlCu4Mg1 (A)	Ti(C,N)	BN	Al ₂ O ₃
Particle size in µm	≤75	≤25	\leq 25	≤0,5

Powders of the starting materials were wet mixed in the laboratory vibratory ball mill to obtain the uniform distribution of the reinforcement particles in the matrix. The mixed powders were then dried in the air. The components were initially compacted at cold state in a die with the diameter of \emptyset 26 mm in the laboratory vertical unidirectional press - with a capacity of 350 kN.

The selected compacting load was sufficient to obtain prepregs which would not crumble and at the same time would not be deformed too much, which would also have the adverse effect on their quality, as the excessive air pressure in the closed pores causes breaking the prepreg up when it is taken out from the die.

The obtained PM compacts were heated to a temperature of 480-500°C and finally extruded - with the extrusion pressure of 500 kN. Bars with the diameter of 8 mm were obtained as the end product. To evaluate the heat treatment effect on corrosion resistance some of the composite materials were hyperquenched for 0.5 h at the temperature of 495°C with the subsequent cooling in water, and were quench aged next for 6 h at 200°C.

The metallographic examinations of the obtained composite material were carried out on the LEICA MEF4A light microscope to investigate the structure of powders and to determine the distribution of the reinforcing particles in the matrix on the cross sections transverse and longitudinal in respect to the extrusion direction of the composite materials. a)







Fig. 1. Morphology of powders: a) aluminum alloy EN AW-AlCu4Mg1(A), b) Ti(C,N), c) Al_2O_3

Density of extruded specimens was estimated with Archimedean principle, by determining the specimen mass and volume, and basing on the apparent loss of weight after immersing the specimen in water.

To determine the corrosion resistance of the EN AW-AlCu4Mg1(A) aluminium alloy and composite materials that differed with the reinforcement content percentage values, corrosion tests were made consisting in registering the anode polarisation curves using the measurement system consisting of the PGP-21 potentiostat working with the Radiometer Copenhagen VoltaMaster 1 software. Specimens of the composite materials featured the examined electrode that were ground and polished with the method used in the practical metallographic chemistry. The inspected surfaces of the specimens were washed with acetone immediately before the examinations. Specimens prepared in this way were tested in the 3% water NaCl solution.

The electrochemical tests were carried out in the threeelectrode glass electrolyser. The platinum electrode was the auxiliary one, and the reference electrode was the saturated calomel electrode. Basing on the potentiodynamical curves the corrosion current i_{cor} was determined, areas close to the equilibrium potential E_{cor} were used for that and Tafel's relationship was used for its evaluation. Making use of the determined values of the corrosion current the corrosion rate v_{cor} , and Rp were calculated for the investigated material in the NaCl environment, using the built-in software function - $,,1^{st}$ Stern Method-Tafel extrapolation".

Photos of the examined surfaces after the corrosion test were taken on the OPTON DSM 940 scanning electron microscope.

3. Results and discussion

The metallographic examinations of the investigated composite materials make it possible to observe the homogeneous distribution of the reinforcing material in the matrix; however, banding of the reinforcing particles parallel to the extrusion direction was noted on the longitudinal microsections (Fig. 2).

Table 3 presents results of density measurements. One can see that for all produced materials density is near to the theoretical one but existing differences indicate presence of porosity.

Examinations of the composite materials on the scanning electron microscope using the EDS add-on before their heat treatment made it possible to reveal occurrences of the Al-Cu-Mg-Mn intermetallic phases' precipitations (Fig. 3). Examinations of these materials in the heat treated state indicate to the reduction of the presence and size of the intermetallic precipitations.

Due to the heat treatment performed the precipitations get dissolved in the solid solution in the hyperquenching process.

As a result of the potentiodynamic tests carried out curves of the current density versus varying potential were obtained. The curves obtained at potential changes in the anodic and cathodic directions confirm that the investigated materials are subjected to pitting corrosion, to which aluminium and its alloys are susceptible. The best electrochemical parameters: E_{cor} , I_{cor} i Rp detemined using the Tafel method (Table 4) are characterisitc of the EN AW-AlCu4Mg1(A)/5%Al₂O₃ composite material. Also a portion of 10% of the reinforcing Al₂O₃ particles cause improvement of the corrosion resistance, compared with the material with no reinforcement.



Fig. 2. Microstructure of longitudinal section of EN AW-AlCu4Mg1(A): a) 15% Al_2O_3 , b) Ti(C,N) composite material, x1000

However, 15% reinforcement portion causes the significant decrease of the corrosion resistance. In case of the composite materials reinforced with the Ti(C,N) particles the best electrochemical parameters are characteristic of the EN AW-AlCu4Mg1(A)/5%Ti(C,N) material. At the 10% and 15% portions of the reinforcing Ti(C,N) particles a slight deterioration of the corrosion resistance occurs, compared with the matrix material.

The same tests made on the composite materials in the precipitation hardened state indicate to the significant improvement of the corrosion resistance in the water NaCl solution. The pitting potential E_{cp} and the re-passivation one E_n were determined from the runs of the potentiodynamic curves and after having compared the corrosion loops widths in the range in which the originated pits can develop, one can state that that the broadest corrosion loops are characteristic of the composite materials with the 15% Al₂O₃ and Ti(C,N) reinforcement particles portion.



Fig. 3. Microstructure of aluminium alloy; before heat treatment, x-ray energy dispersive spectrum for intermetallic precipitations, after heat treatment

The pitting potential values grow along with the increase of the volume portion of the reinforcing particles. The exemplary microphotographs of the examined specimens' surfaces after the corrosion tests in the precipitation hardened state show (Fig.4) pits and crack locations close to the pits, confirming the corrosion test results. a)



Fig. 4. Surface of the composite materials in the precipitation hardened state after the corrosion tests: a) EN AW-AlCu4Mg1(A) / 10%Al₂O₃, b) EN AW-AlCu4Mg1(A) / 10%Ti(C,N)

Table 3.

Density measured for investigated materials

Having compared breadth of the corrosion loops (i.e., parameters E_n and E_{cp} in the range in which new pits cannot develop; however, in those already existing corrosion processes may continue), and also the inclination angles and height of these loops, one can infer that that the worst corrosion loops compared to the material without the reinforcement are characteristic of the composite materials with the 15% Al₂O₃ reinforcement particles portion. The pitting potential values increase along with the increase of the volume portion of the reinforcing particles in the matrix.

Breadth of these loops decreased after the heat treatment, just like the pitting potential E_n and the re-passivation one E_{cp} , heightand inclination angle of these loops decreased too, which also attests to the positive effect of the heat treatment on the corrosion resistance of the investigated materials (Fig. 5).

4. Conclusions

Basing on the structural examinations carried out of the composite materials with the EN AW-AlCu4Mg1(A) aluminium alloy matrix reinforced with the Al_2O_3 and Ti(C,N) particles the homogeneity of their distribution in the matrix was revealed, as well as the fact that during their extrusion the directed structure develops oriented according to the extrusion direction.

The heat treatment employed makes it possible to reduce significantly the sizes of the intermetallic phases' precipitations and results in a more homogeneous matrix structure. The influence was observed of the heat treatment carried out on the corrosion resistance of the investigated composite materials. Introducing the Al_2O_3 reinforcing particles into the matrix causes improvement of the corrosion resistance of the investigated materials.

Material	Theoretical density, g/cm ³	Measured density, g/cm ³	Ratio of real density to the theoretical density, %		
EN AW-Al Cu4Mg1(A)	2.78	2.76	99.28		
EN AW- Al Cu4Mg1(A)/5%Ti(C,N)	2.9	2.88	99.31		
EN AW- Al Cu4Mg1(A)/10%Ti(C,N)	3.02	2.98	98.67		
EN AW- Al Cu4Mg1(A)/15%Ti(C,N)	3.14	3.09	98.4		
EN AW- Al Cu4Mg1(A)/5%Al ₂ O ₃	2.86	2.79	98.23		
EN AW- Al Cu4Mg1(A)/10% Al ₂ O ₃	2.89	2.8	96.88		
EN AW- Al Cu4Mg1(A)/15% Al ₂ O ₃	2.95	2.87	97.28		

Table 4.

Electro-chemical parameters of the matrix from the EN AW-AlCu4Mg1(A) aluminium alloy and composite materials reinforced with the Al_2O_3 and Ti(C,N) particles in the states before the heat treatment and after precipitation hardening after their corrosion tests in the 3% NaCl solution

The investigated materials in the state before the heat treatment (A) and in the precipitation hardened state (B)												
Mass fraction of the reinforcing particles, %		Corrosion compotential, $E_{cor}[mV]$		Corrosio I _{cor} , m	Corrosion current, I _{cor} , mA/cm ²		Polarization resistance, Rp, kΩ/cm ²		Pitting potential, E _{cp} , mV		Repassivation potential, E _n , mV	
Al ₂ O ₃	Ti(C,N)	А	В	А	В	А	В	А	В	А	В	
EN AW-Al	Cu4Mg1(A)	-686	-644	0.0154	0.0019	0.3828	5.85	-646	-629	-712	-705	
5	-	-669	-633	0.0089	0.0001	0.6010	33.7	-641	-618	-701	-695	
10	-	-683	-638	0.0148	0.0011	0.4246	15.3	-644	-620	-707	-700	
15	-	-693	-662	0.0225	0.0023	0.1300	2.45	-651	-631	-720	-714	
-	5	-678	-634	0.0073	0.0017	0.6090	7.25	-625	-630	-712	-706	
-	10	-706	-675	0.0190	0.0044	0.2470	3.48	-628	-611	-704	-717	
-	15	-714	-683	0.0235	0.0047	0.0875	1.67	-644	-582	-705	-725	



Fig. 5. Potentiodynamic curve for EN AW-Al Cu4Mg1(A) and aluminum alloy composite materials tested in 3% NaCl: a) Ti(C,N), b) Al₂O₃, after the heat treatment

At the 5% and 10% portions of the reinforcing particles this resistance is better, and at their 15% portion a slight deterioration of the corrosion resistance occurs, compared with the matrix material. In case of the composite materials reinforced with the

Ti(C,N) particles, also at the 5% portion the corrosion resistance improves compared to the matrix material corrosion resistance; whereas, at the 10% and 15% portions this resistance gets slightly worse.

Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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