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INFLUENCE OF LASER REMELTING AT CRYOGENIC CONDITIONS ON CORROSION RESISTANCE OF NON-FERROUS ALLOYS

ABSTRACT

The main reason for laser remelting of the components made of aluminium, copper and titanium alloys is to obtain high hardness and corrosion resistance at the surface for longer lifetime as result of the rapid solidification. The final microstructure, phase composition and properties of aluminium, copper and titanium alloys depend on the laser process parameters and obviously on the nature of the equilibrium system.

The effect of laser surface remelting at cryogenic conditions on the microstructure and corrosion characteristics of the AlSi13Mg1CuNi, SUPERSTON and Ti-6Al-4V alloys are presented. The beneficial effects of laser treatment on the microstructure and corrosion behaviour of those alloys used for different products are observed.

Key words: *aluminium, copper and titanium alloys, laser treatment, corrosion*

INTRODUCTION

Aluminium, copper and titanium alloys are, beside iron based materials, most often alloys used in mechanical engineering, automotive, shipbuilding, aircraft and aerospace industries. Aluminium alloys and in particular multicomponent aluminium alloys containing silicon are used for car and aircraft engines' bodies and pistons. Wide area of copper alloys application is manufacturing of propellers used for motor-boats and cargo or passenger ships. Titanium alloys, which are highly bio-compatible with human's body materials, are used in orthopaedics and dentistry for endo-prostheses and dentures. The problem is that the above mentioned alloys are not always sufficiently resistant to friction, corrosion or - commonly observed simultaneous occurrence of the phenomena - tribocorrosion.

Susceptibility of alloys to destructive impact of environment can be improved with classical methods of heat treatment used for bulk or limited to surface area. It can be also improved with advanced surface engineering methods including laser surface remelting at cryogenic conditions [1-4].

The purpose of this paper is to asses an influence of laser remelting at cryogenic conditions on selected aluminium, copper and titanium alloys corrosion resistance.

MATERIALS AND INVESTIGATION METHODOLOGY

The EN AC- AlSi12CuNiMg (PN EN-573.1), SUPERSTON CC212E (PN EN 1982, category Cu4 according to Polish Register of Ships) and Ti-6Al-4V (Grade 5, ISO 5832/3) were assigned for researches.

After laser remelting at cryogenic conditions of the EN AC- AlSi12CuNiMg alloy (generally used for the combustion engine pistons) were obtained repeated increase of hardness and wear resistance [5, 6]. That treatment caused also the significant increase of hardness and cavitation resistance of the SUPERSTON alloy in comparison to the base material [7, 8]. For the Ti-6Al-4V alloy laser remelting obtained significant increase of tribocorrosion properties [9].

Detailed description of the laser remelting at cryogenic conditions process was shown in articles [3, 4]. In this article laser remelting was done by the molecular CO_2 TRUMPF laser TLF 6000 turbo in Kielce University of Technology. During that process the specimens were immersed in liquid nitrogen and distance from laser head to sample was about 10 mm.

Laser remelting of the: EN AC- AlSi12CuNiMg , SUPERSTON and Ti-6Al-4V alloys were done by non-continuous laser beam, with 30 Hz frequency and parameters which are shown in table 1.

Table 1. Parameters of the laser remelting process

Type of material	Number of sample	Laser beam dimension [mm]	Power of beam [W]	Scanning velocity [m/min]	Power density [W/cm ²]
EN AC- AlSi12CuNiMg	21A	$\varnothing 3$	1500	1.0	21221
	72C	1x20	6000	1.0	30000
SUPERSTON	12	1x20	4000	1.0	20000
	16			0.5	10000
	14		6000	1.0	30000
	20			0.5	15000
Ti-6Al-4V	1	1x20	3000	10	15000
	2		4000		20000
	3		5000		25000
	4		6000		30000
	5		5000	0.5	12500
	6		6000		15000

Corrosion investigations were carried out for specimens showed in table 1 and for reference base material (specimens MR and SS).

After corrosion test the surface specimens microstructure were observed by scanning electron microscope (SEM) with different magnifications.

INVESTIGATION RESULTS AND DISCUSSION

In corrosion test of the EN AC- AlSi12CuNiMg alloy was used 0.01 M water solution of sulphuric acid, for the SUPERSTON alloy – 3%NaCl, for the Ti-6Al-4V alloy – Ringer solution (8.6g NaCl, 0.3g KCl, 0.33g CaCl_2 in 1 dm^3 water). The specimens were inserted in the glass container including 0.5 dm^3 of solution. Reference electrode was saturated calomel electrode and the auxiliary electrode was titanium coated with platinum layer. The investigations were carried out in 25 ± 1 °C temperature. The electrochemical measurements were achieved by the Atlas 9131 Electrochemical Interface and Atlas 9121 Frequency Response Analyzer. During the corrosion test the solution was mixed by magnetic stirrer with 50 rpm/min velocity.

Impedance spectra were recorded with the following settings of the instrument: ac amplitude: 20 mV, frequency range: from 100 kHz to value lower than 0.1 Hz, logarithmic frequency shift. During polarisation tests 10 mV steps of electrochemical potential were used and the values were recorded at the end of each step. Potential sweep rate was: 10 mV/min. At the beginning of each test potential was set to corrosion potential value and polarisation was carried out in cathodic direction to -250 mV value measured versus corrosion potential. After that the specimens were polarised to +250 mV value vs. corrosion potential.

Specimens made of EN AC- AlSi12CuNiMg alloy were first 0.5 h exposed, and after that during 0.5 h impedance tests were carried out. Then polarisation tests were started. For data analysis *impfit* and *elfit2* computer programs were used [10].

Impedance spectra were modeled with an equivalent electric circuit presented in Fig. 1.

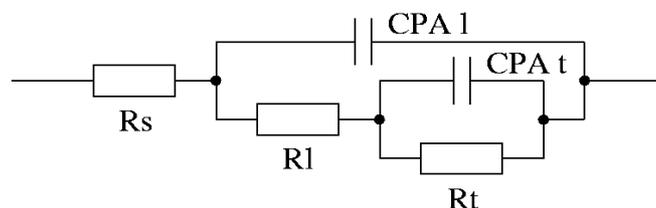


Fig. 1. Equivalent electric circuit used for impedance spectra analysis

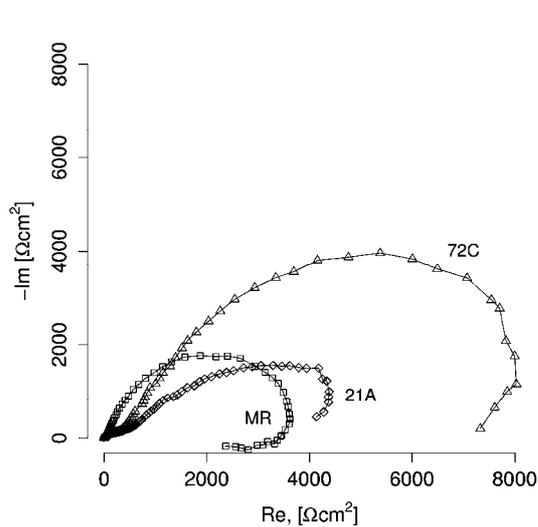
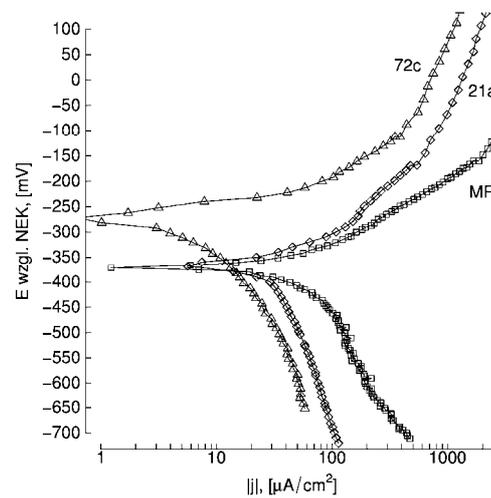
R_s value is used as an equivalent of electrolyte resistance presented between Habber-Luggin capillary tube and the specimen's surface - this value is negligibly low in presented tests. This value is increased with resistance of the outer part of surface which acts as barrier - electric insulator. The subcircuit assembled of resistance R_t and constant phase element (capacitance) CPA_t creates semicircle in low-frequency part of Nyquist diagram. These elements characterize electric properties of a surface layer (porous layer) and are frequently interpreted as resistance and capacitance of pores. The values of R_t and CPA_t usually depend on chemical heterogeneity of surface and diffusion processes proceeding close to the surface. The R_t and CPA_t are properties of charge transfer through electric double layer presented on surface of tested sample. The R_t and CPA_t are presented as semicircle in high-frequency part of Nyquist diagram.

In the table 2 and Fig. 2 are presented properties of numerical value and impedance curves determined during corrosion test of EN AC- AlSi12CuNiMg alloy.

Table 2. The value appointed during impedance investigation of the EN AC-*AlSi12CuNiMg* alloy

Number of specimen	R_s [Ωcm^2]	R_l [Ωcm^2]	CPA_l [nF/cm ²]	a_1	R_t [Ωcm^2]	CPA_t [mF/cm ²]	a_t
MR	0	31	75	0,82	4020	3.8	0.86
21A	0	417	35	0,73	6376	0.16	0.57
72C	6	232	201	0,90	13752	1.0	0.67

The potentiostatic curves analysed with the help of the elfit2 program used model electrochemical process progressed with activation and diffusivity control. The findings are shown in table. 3.

**Fig. 2.** Impedance curves of the EN AC-*AlSi12CuNiMg* alloy**Fig. 3.** Potentiostatic curves of the EN AC-*AlSi12CuNiMg* alloy**Table 3.** E_c and j_{kor} appointed for EN AC-*AlSi12CuNiMg* alloy

Number of specimen	E_c [mV]	J_{kor} [Ma/cm ²]	B [mV]	R_p [Ωcm^2]
MR	-371	45	31	750
21A	-379	47	50	1276
72C	-282	6,8	25	3881

The surface microstructure (SEM) of the EN AC-*AlSi12CuNiMg* alloy after corrosion test were performed for MR, 21A and 72C specimens.

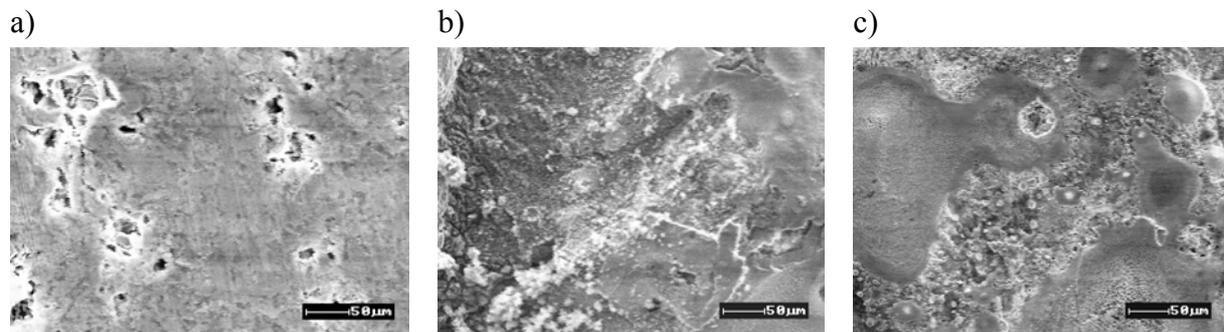


Fig. 4. Surface microstructure (SEM) of the laser remelted EN AC-AISi12CuNiMg alloy after corrosion test: a – specimen MR, b – specimen 21A, c – specimen 72C

The potentiostatic curves after corrosion test of the SUPERSTONE alloy are shown in the Fig. 5, while numerical values of corrosion potential (E_c) and corrosion current density (J_{kor}) are compiled in table 4.

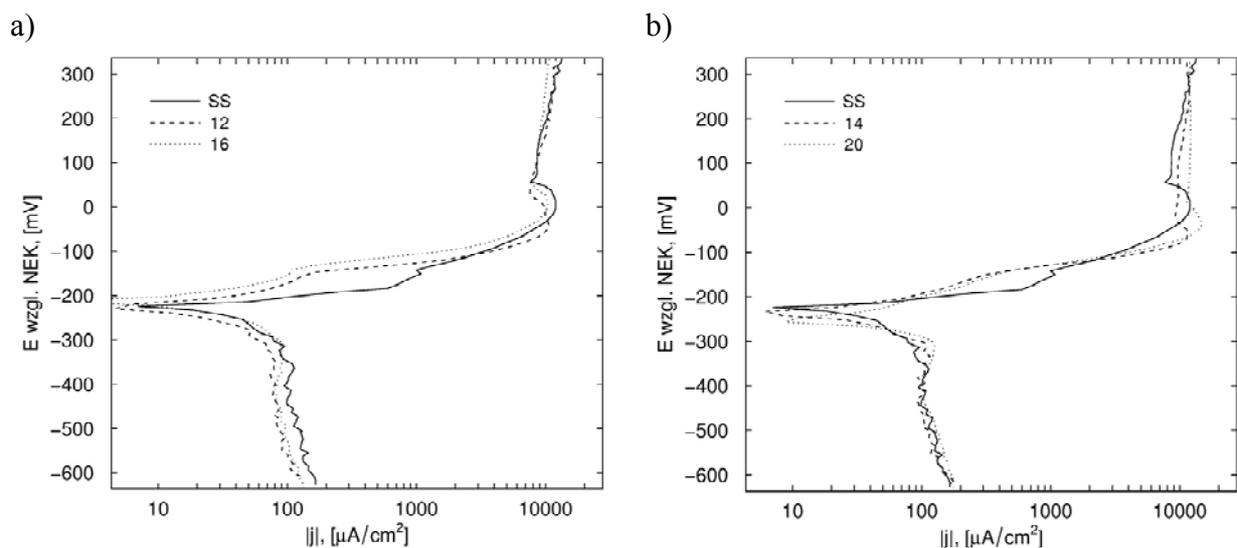


Fig. 5. Potentiostatic curves of the SUPERSTONE alloy after remelting at cryogenic conditions, specimens. a – No 12 and 16, b – No 14 and 20, SS – base material

Table 4. E_c and J_{kor} appointed for SUPERSTONE alloy

Number of specimens	E_c [mV]	R_p [Ωcm^2]	J_{kor} [$\mu\text{A}/\text{cm}^2$]
SS (base material)	- 220	385	51.95
12 (4 kW; 1.0 m/min)	- 225	934	21.41
16 (4 kW; 0.5 m/min)	- 210	1030,1	19.40
14 (6 kW; 1.0 m/min)	- 235	643	31.10
20 (6kW; 0.5 m/min)	- 250	478,3	41.81

After corrosion tests the surface microstructure of casted and laser remelted specimens of the SUPERSTON alloy were observed. Views of the surface microstructure chosen specimens after corrosion test are presented in Fig. 6.

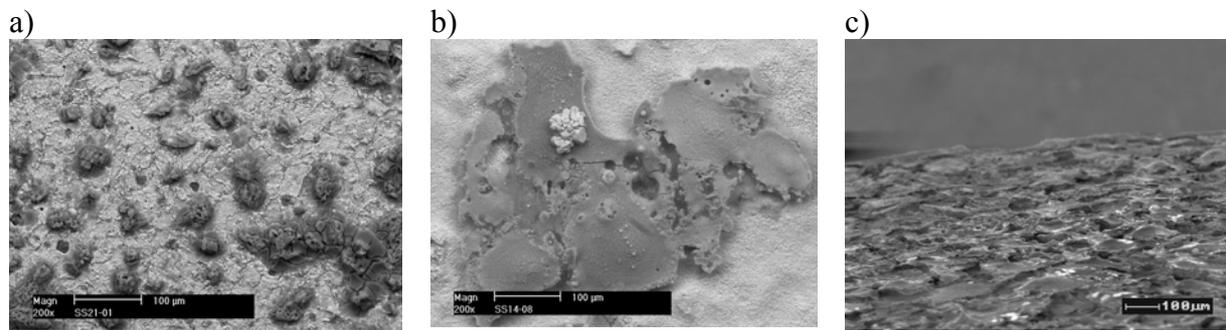


Fig. 6. Surface microstructure of the laser remelted SUPERSTON alloy after corrosion test:
a - sample SS, b - sample 14, c - sample 16 (spatial view)

Polarization curves obtained for Ti-6Al-4V alloy in Ringer solution is shown in Fig. 7. The surface microstructures of chosen titanium specimens after corrosion test are presented in Fig. 8.

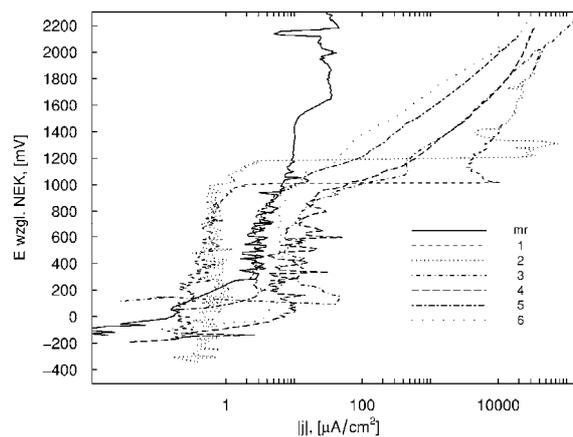


Fig. 7. Potentiostatic curves of the Ti-6Al-4V alloy after laser remelting at cryogenic conditions specimens: No 1, No 2, No 3, No 4, No 5, No 6 and mr- base material

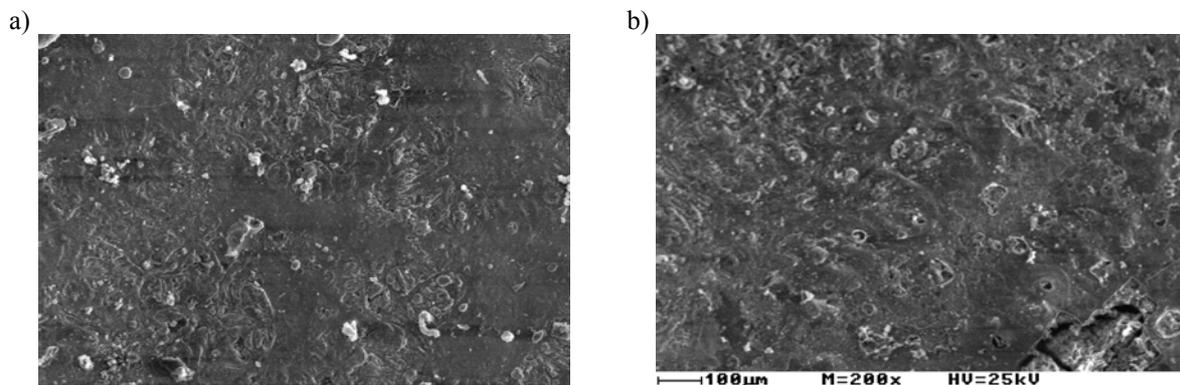


Fig. 8. Surface microstructure (SEM) of the laser remelted Ti-6Al-4V alloy after corrosion test, specimens:
a – No 2, b – No 3

Received results of corrosion investigations show that laser remelting at cryogenic conditions caused increase of corrosion resistance of explored materials. In these cases deciding matter had remelting process specific and microstructure changes caused the laser treatment.

Laser remelting at cryogenic conditions led to the few effects. The first of them is changing the microstructure alloys on the ultra fine-grained, nanocrystalline or amorphous microstructure. The second one effect is inhibition intermetallic phases and forming supersaturated solutions. It is the main causes increased corrosion resistant of the aluminum and cooper alloys. Ultra fast solidification of liquid solution caused formation of zonal structure in the layer. Different solidification temperatures of the metallic components in investigated alloys are the cause, that: in the surface zone solidified phases of the highest crystallization temperature and in the center zone solidified supersaturated solutions. These characteristics could expect for all multiphase alloys. Ultra fast crystallization caused high internal stresses, in case of titanium alloy additionally could precede martensite transformation. In consequence could appear the surface cracks which are observed in titanium alloys [11]. The corrosion solution which penetrates to the surface cracks could caused the pH local decrease and reduced of corrosion resistance of laser remelting titanium alloys.

CONCLUSIONS

Laser remelting at cryogenic conditions generally resulted in increase of the corrosion resistance of the aluminum, copper and titanium alloys.

Increase of corrosion resistance after laser remelting investigated materials is result forming ultra fine-grained microstructure in the remelted layers, consisted of supersaturated solid solutions and small quantity intermetallic phases, limited in this way formed possibility of corrosion cells.

REFERENCES

1. Tang H.C., Cheng F.T., Man H.C.: Effect of surface melting on corrosion and cavitation erosion behaviors of manganese-nickel-aluminium bronze, *Materials Science and Engineering A* 373 (2004), 195 – 203.
2. Serbiński W., Olive J.M., Rudnicki J.: Laser surface treatment of aluminium-silicon alloy at cryogenic conditions. *Advances in Materials Science* Vol. 3, nr 1(3), (2003), 51-59.
3. Serbiński W., Zieliński A., Dziadoń A., Wierzchoń T.: Structural transformations in syrface areaof Al-Si alloy caused with laser remelting under low temperature conditions. *Inżynieria Materiałowa*, 2005, vol. 26, nr 5, 291-302.
4. Jazdzewska M., Zieliński A., Dziadoń A.: The possibility of and use of laser treatment to improve the behaviour of the Ti-6Al-4V alloy. *Inżynieria Biomateriałów* 9 (2006) 121-123.

5. Skalski I, Serbiński W., Majkowska B.: Corrosion tests of laser remelted AlSi13Mg1CuNi alloy exposed in 0.01M H₂SO₄ water solution. *Materiały i Technologie* 2(2) 2004, 159-162.
6. Zieliński A., Serbiński W., Kamiński J., Wierzchoń T.: Laser remelting of highly precolled Al-Si alloys as a method of their corrosion resistance increasing. *Ochrona przed Korozją* 47 (2004) nr 11s/A, 72-75.
7. Majkowska B., Skalski I., Serbiński W.: Microstructural aspects of corrosion of the SUPERSTON alloy after laser treatment. *Advances in Materials Science*, vol. 7, iss. 2=12 (2007), 141-146.
8. Serbiński W., Majkowska B.: Microstructure and corrosion properties of the laser treated SUPERSTON alloy. *Journal of Achievements in Materials and Manufacturing Engineering*, vol. 18, iss. 2/2 (2006), pp. 415-418
9. Zieliński A., Jażdżewska M., Narożniak-Łuksza A., Serbiński W.: Surface structure and properties of Ti6Al4V alloy laser melted at cryogenic conditions. *Journal of Achievements in Materials and Manufacturing Engineering* 17 (2006) 423-426.
10. Skalski I.: Computer software for polarisation data analysis. CTO's internal publication, RO-00/T-049, 2000.
11. Jażdżewska M., Zieliński A., Skalski I., Dziadoń A.:_New laser-enhanced surface treatment of Ti bioalloy. *Advances in Materials Science* 7 (2007) 295-299.