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Properties of Al - Ga alloys during cathodic polarization in NaF solution

ABSTRACT

In this paper, the electrochemical properties of high - purity aluminium with the addition of small amounts of gallium at high cathodic potentials have been investigated. The anodic current was followed through time in order to determine the quantity of charge needed for the formed substances oxidation. Anodic current responses for the period of 1 s were recorded. Time responses for the cathodic and anodic currents were recorded and showed in characteristic diagrams. The range of low and high cathodic potentials (LCP, HCP) was defined for all samples. For the experimental work, standard electrochemical cell with saturated calomel electrode (SCE) and platinum counter electrode were used. The solution 2 M NaF was used for this work.

Keywords: *Al-Ga alloy, Cathodic polarization, Aluminium activation, NaF solution, Hydration potential.*

1. INTRODUCTION

Poor mechanical properties of pure aluminium (low strength and hardness), decrease its usage as a construction material. Corrosion processes of high-purity aluminium (99.999 wt% - 5N), were intensively investigated [1,2]. However, by adding the selected elements to pure aluminium, aforesaid properties can be improved and the usage of such alloys widen. These added elements, although improving mechanical properties can weaken aluminium's characteristic property – it's resistance to corrosion. Thus, alloys become more electrochemically active. Lately, the focus has been significantly turned to the certain number of aluminium alloys where the aluminium is electrochemically active; e. g. alloyed with gallium, indium, tin, bismuth or with the combination of mentioned elements. The goal is to obtain materials suitable for sacrificial anodes and chemical power sources [3-5]. Alloying elements affect the active places formation on the basic metal and the extracted alloying element grain boundaries, which improves the anodic process [6].

2. EXPERIMENTAL WORK

Al–Ga binary alloys were obtained in corporation with Alcan International Ltd. The content of gallium as an alloying component was: 0.01; 0.02; 0.05; 0.1; 0.2 and 2.6 wt% in high-purity aluminum (99.999 wt% - 5N) samples.

The content of gallium and other elements in alloys was analyzed with the use of optical emission spectrometry (Fig. 1).

Figure 1 - Optical emission spectrometer ARL - MA (simultaneous quantometer)

The alloys samples were turned into electrodes (1 cm^3 cubes), while the electrode contact was generated through aluminum contact wire. The

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sample was isolated with epoxy resin, leaving only one face (~1 cm^2) open for the electrolyte contact. Before each experiment, free side was mechanically polished to a mirror finish then treated with oxide removing solution (1.8 wt% CrO_3 + 7 wt% H_3PO_4) at 80 °C, for 1 minute. After rinsing in distilled water, it was left in air to obtain its “natural” oxide layer, before immersing into solution. During experiment conduction, a standard electrochemical three electrode cell was used. It consisted of working electrode, platinum counter electrode and referent saturated calomel electrode (SCE). The solution used in experiment was 2 M NaF.

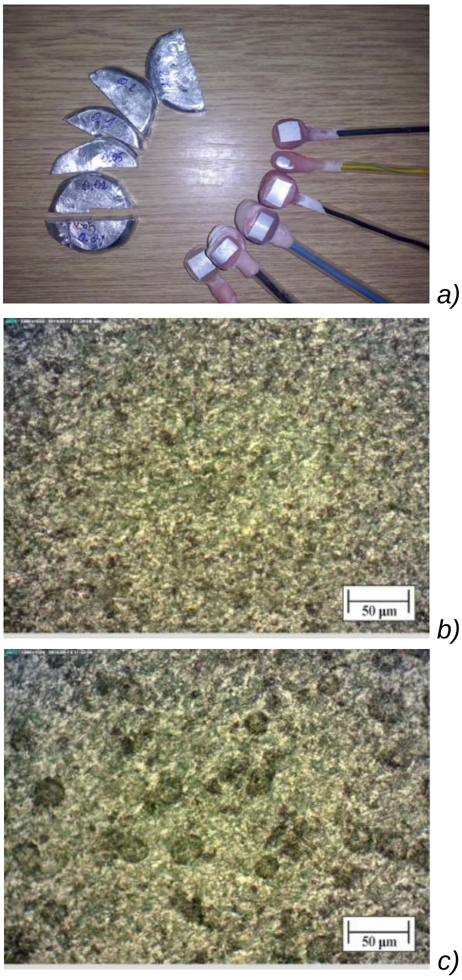


Figure 2 - a) 5N Al - Ga working electrodes and alloy samples with gallium content given as following (from bottom to top): Al - 0.01 wt% Ga; Al - 0.02 wt% Ga; Al - 0.05 wt% Ga; Al - 0.1 wt% Ga; Al - 0.2 wt% Ga; Al - 2.6 wt% Ga; b) Metallographic structure for 5N Al - 0.01 wt% Ga alloy sample; c) Metallographic structure for 5N Al - 2.6 wt% Ga alloy sample

The experiment’s working temperature has been held at 25 ± 0.1 °C. The measurements were conducted with a computer controlled potentiostat PAR M273A.

The shape of the working electrodes along with metallographic microstructures of two chosen Al-Ga alloy samples was given in Fig.2. The suspension for microstructure development (0.5 cm^3 40 wt% HF + 100 cm^3 H_2O), was used as a standard metallographic etching agent for aluminum and aluminum-based alloys.

The purpose of measurements was to determine the behavior of certain Al-Ga alloys at high cathodic potentials. The idea was to estimate the quantity of products formed on the surface in the two ranges of cathodic potentials; before and after complete hydration of the oxide layer. As it is known, when aluminum is under cathodic polarization, hydration of the oxide takes place at some negative potentials, because of the increased concentration of OH ions produced in the process of hydrogen evolution from water [7]. Moreover, the anodic current that occurs after cathodic polarization was observed, as well as the estimation of the amount of substances oxidized through the potential regression to values somewhat more positive than the open circuit potential.

After the open circuit potential (OCP) value is reached, the chosen cathodic potential was set. Current-time responses were recorded directly with the potentiostat through the computer operating with a suitable curve adjustment and response integration software.

2.1. Measuring methods

For the Al-Ga alloys cathodic behavior analysis, two electrochemical methods were used: the potentiostatic pulse method and the cyclic voltammetry method. The dependence of open circuit potential (OCP) on gallium content in alloys at pH values from 3 to 10, was monitored through the period of 36 hours.

The analysis of time dependence of the cathodic current density on the pulsing electrode potential from the OCP values to -2000 mV versus SCE with pulse duration of 1 s, was conducted by potentiostatic pulse method.

The linear alteration of current in time was monitored by cyclic voltammetry method in order to explore the dependence of oxide layer hydration outset on gallium content in aluminum alloy. The potential deviation shifted from values somewhat more positive than the OCP potential in negative direction down to -2000 mV versus SCE and back, with a potential sweep rate of 0.5 mV s^{-1}. The current responses were converted directly into logarithmic scale in order to obtain Tafel dependence plots.

With a low potential sweep rate, the stationary state was simulated at every potential. Out of these dependences, Tafel parameters, E_{corr}, i_{corr}, E_h and i_h were defined, thus providing the insight to corrosion behavior of Al-Ga alloys.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential (OCP)

The OCP testing was conducted in 2 M NaF solution in pH interval ranging from 3 to 10. *E* vs. time curves for pure aluminium and different Ga alloyed samples recorded at pH 6 are shown in Fig. 3.

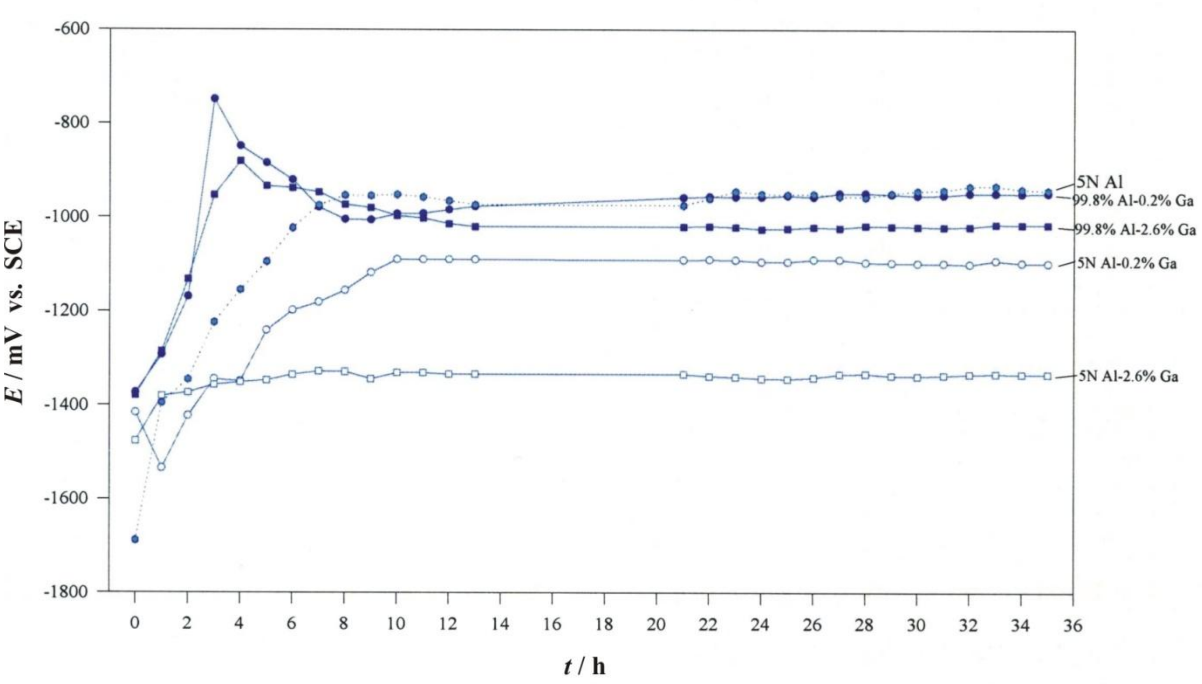


Figure 3 - Open circuit potential (E_{OCP}) versus time diagram for 5N Al and 5N Al with 0.2 and 2.6 wt% Ga; 99.8 wt% Al with 0.2 and 2.6 wt% Ga; in 2M NaF at pH=6.

The monitoring showed negative potential trend in relation to OCP values of high-purity aluminum. For alloy with gallium content of 0.2 wt% at pH = 6, OCP is -1100 mV, while for the alloy with gallium content of 2.6 wt%, the value is -1320 mV.

The time necessary for OCP stabilization was around 10 h.

More negative value of OCP for Al-Ga alloys can be assigned to more active anodic component of corrosion process.

This OCP negative trend phenomenon is more expressed in chloride solutions [8].

3.2. Potentiostatic pulse measurements

3.2.1. Chatodic current - time responses

Typical current - time responses to the potential pulse from E = -1600 mV for 5N Al - 0.01 wt% Ga, with pulse duration of 1 s in 2 M NaF solution, are shown in Fig. 4.

It is shown that with the potential deviation diverging in cathodic direction, cathodic current occurs, while the potential returning to near OCP value induces anodic current.

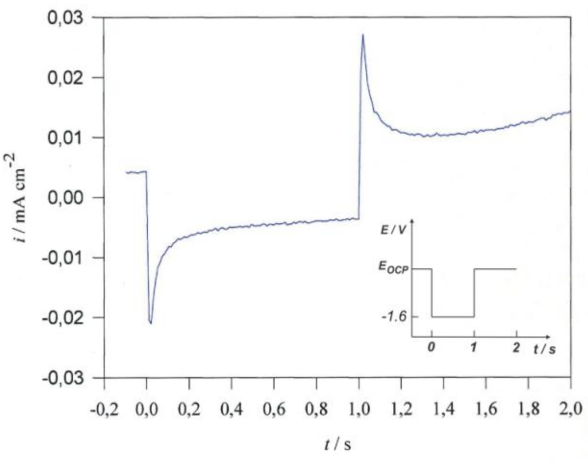
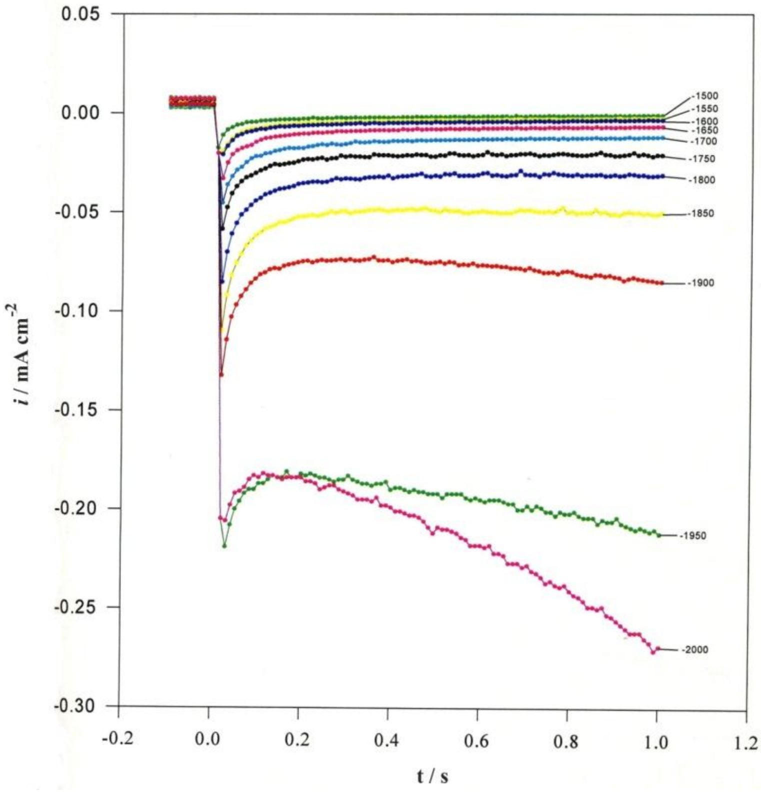
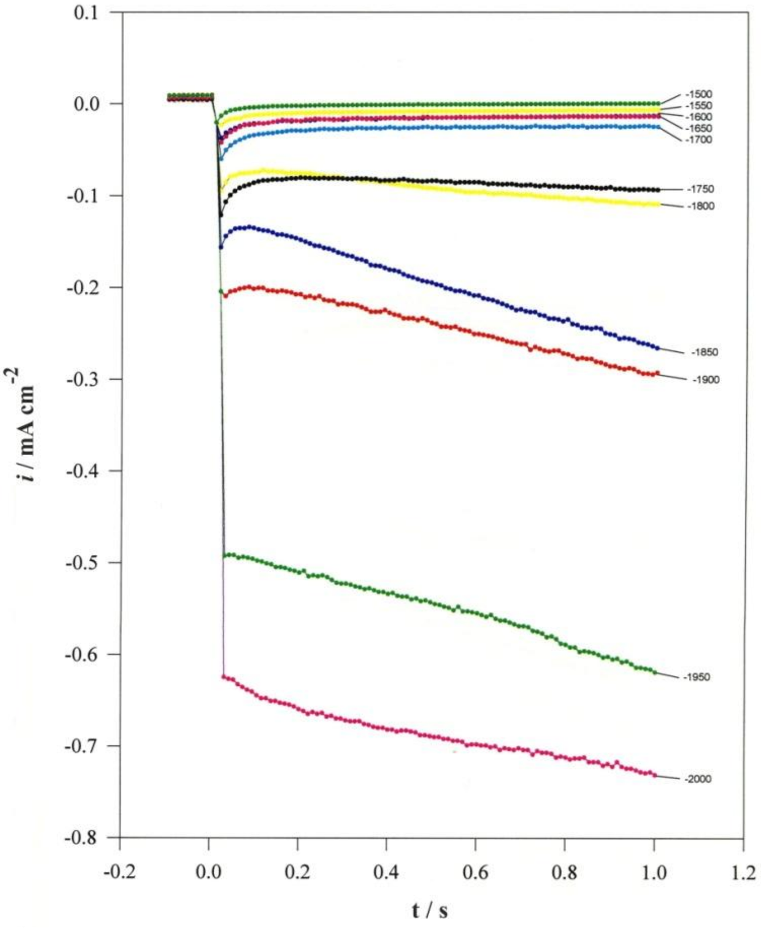


Figure 4 - Current - time responses to the potential pulse from E = -1600 mV for 5N Al - 0.01 wt% Ga, with pulse duration of 1 s in 2M NaF solution

Characteristic current - time response sequences for the increasing series of cathodic pulses by 50 mV (ranging from -1200 to -2000 mV) for all Al-Ga alloys, are shown in Fig. 5.


0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
i / mA cm-2
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
t / s
-1500
-1550
-1600
-1650
-1700
-1750
-1800
-1850
-1900
-1950
-2000

5a)


0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
i / mA cm-2
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
t / s
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-1600
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-1700
-1750
-1800
-1850
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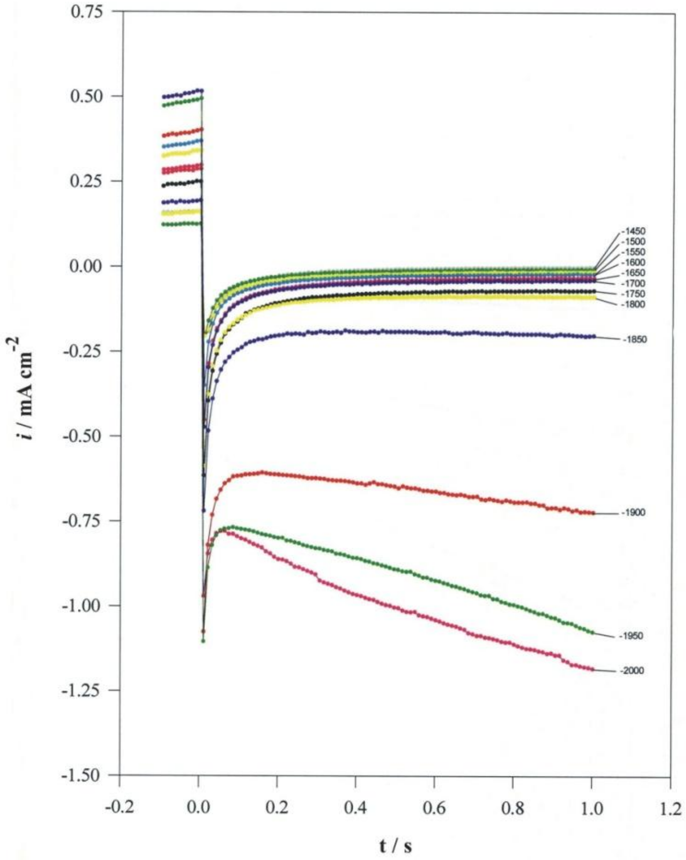
-1950
-2000

5b)


0.75
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-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
i / mA cm^{-2}
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
t / s
-1450
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-1550
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-1700
-1750
-1800
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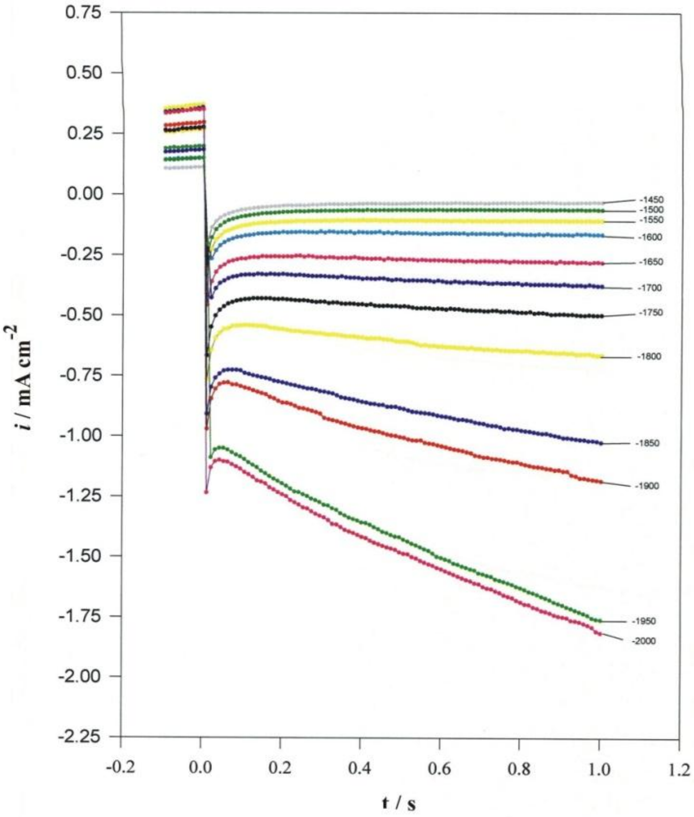
-1900
-1950
-2000

5c)


0.75
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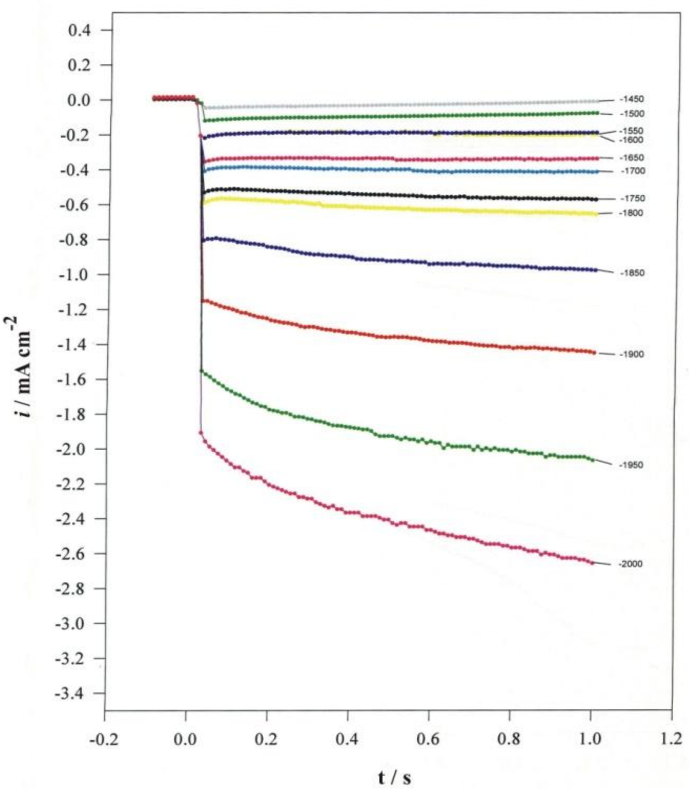
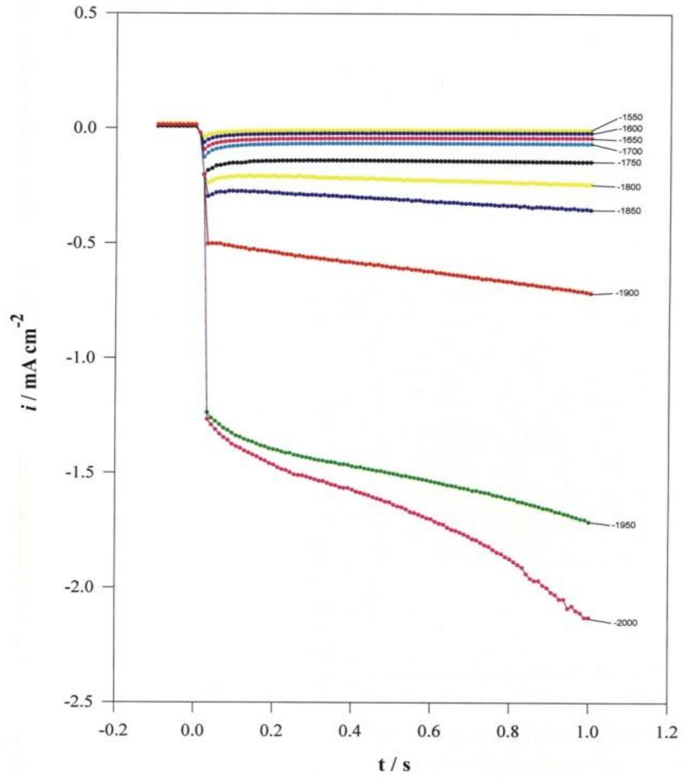
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-1.50
-1.75
-2.00
-2.25
i / mA cm^{-2}
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
t / s
-1450
-1500
-1550
-1600
-1650
-1700
-1750
-1800
-1850
-1900
-1950
-2000

5d)



5e)



5f)

Figure 5 - Characteristic chatodic current-time responses to the potential pulse from E_{OCP} to different negative values (shown on diagrams) and back, for pulse duration time of 1s, for 5N Al - Ga alloys in 2M NaF solution: a) 5N Al - 0.01 wt% Ga; b) Al - 0.02 wt% Ga; c) Al - 0.05 wt% Ga; d) Al - 0.1 wt% Ga; e) Al - 0.2 wt% Ga; f) Al - 2.6 wt% Ga.

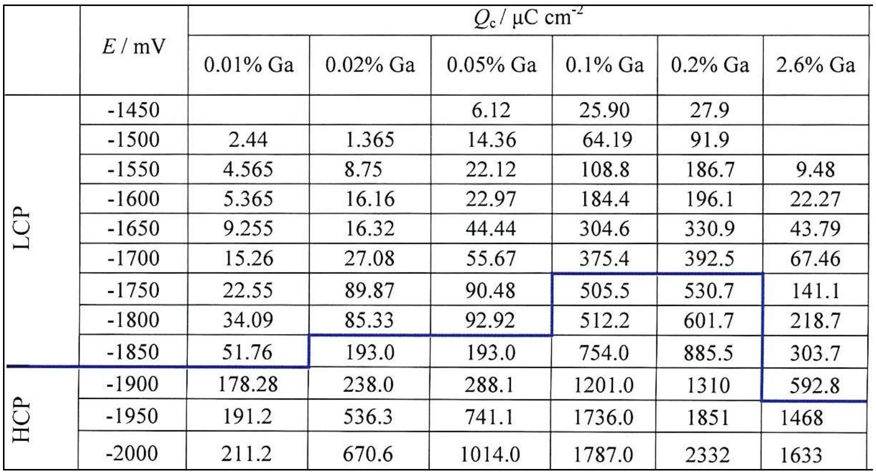
The potential values at which the curve does not follow the exponential dependence, probably indicate the start of hydration. Fluoride ions shift the melting potential towards negative direction due to the “spending” of fluoride ions in oxide layer on aluminum ions located on metal/oxide inner surface, during the aluminum fluoride forming process [9].

The more negative the potential is, the hydrogen release from the water increases more intensively, leaving behind the equivalent amount of OH^- ions which attack the oxide surface. The consequence of that attack is the oxide layer hydration. Hunter et al. [10] have discovered that with the potential shifting in negative direction on the surface of Al-Ga alloys, superactivity appears. Superactivity is caused by the presence of solid state Ga only.

From the results shown in Fig. 5, i.e. with the potential shifting in cathodic direction, two significantly different potential ranges can be perceived. The low cathodic potential range (LCP), at which the initial current peaks are stable and the high cathodic potential range (HCP), at which some complex current-time dependences are noted.

The area below the cathodic current-time response curve represents the quantity of the reduction charge (Q_c), for every alloy at pulse duration of 1s. The obtained values are shown in Table 1.

Table 1 - The values for the quantity of reduction spent charge “Q_C” for all 5N Al - Ga alloys for every cathodic potential deviation at pulse duration of 1 s; in 2M NaF solution

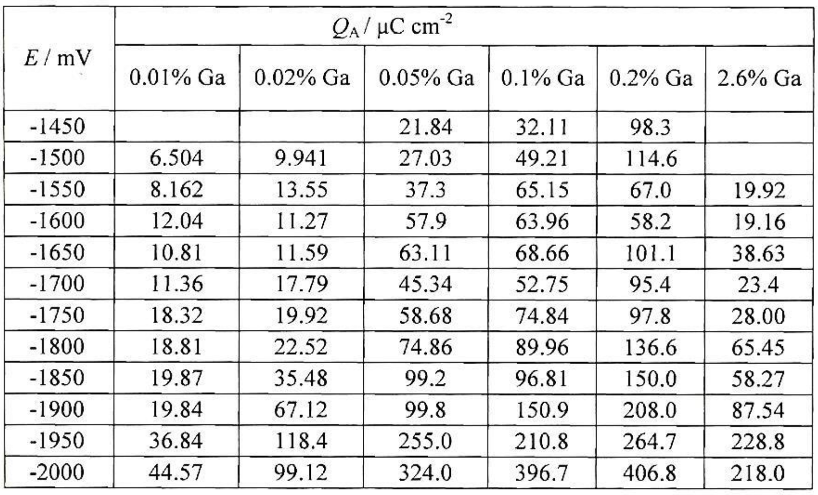


	E / mV	Q_c / μC cm^{-2}					
		0.01% Ga	0.02% Ga	0.05% Ga	0.1% Ga	0.2% Ga	2.6% Ga
LCP	-1450			6.12	25.90	27.9	
	-1500	2.44	1.365	14.36	64.19	91.9	
	-1550	4.565	8.75	22.12	108.8	186.7	9.48
	-1600	5.365	16.16	22.97	184.4	196.1	22.27
	-1650	9.255	16.32	44.44	304.6	330.9	43.79
	-1700	15.26	27.08	55.67	375.4	392.5	67.46
	-1750	22.55	89.87	90.48	505.5	530.7	141.1
	-1800	34.09	85.33	92.92	512.2	601.7	218.7
	-1850	51.76	193.0	193.0	754.0	885.5	303.7
HCP	-1900	178.28	238.0	288.1	1201.0	1310	592.8
	-1950	191.2	536.3	741.1	1736.0	1851	1468
	-2000	211.2	670.6	1014.0	1787.0	2332	1633

3.2.2. Anodic current - time responses

Termination of the cathodic pulse and the potential return to the OCP values results in anodic current quantity of charge spent on the oxidation of substance (Q_A). The values for Q_A charge are given in Table 2.

Table 2 - The values for the “Q_A” charge for 5N Al - Ga alloys obtained by the integration of current-time responses after return of the potential to the rest value; in 2M NaF solution



E / mV	Q_A / μC cm^{-2}					
	0.01% Ga	0.02% Ga	0.05% Ga	0.1% Ga	0.2% Ga	2.6% Ga
-1450			21.84	32.11	98.3	
-1500	6.504	9.941	27.03	49.21	114.6	
-1550	8.162	13.55	37.3	65.15	67.0	19.92
-1600	12.04	11.27	57.9	63.96	58.2	19.16
-1650	10.81	11.59	63.11	68.66	101.1	38.63
-1700	11.36	17.79	45.34	52.75	95.4	23.4
-1750	18.32	19.92	58.68	74.84	97.8	28.00
-1800	18.81	22.52	74.86	89.96	136.6	65.45
-1850	19.87	35.48	99.2	96.81	150.0	58.27
-1900	19.84	67.12	99.8	150.9	208.0	87.54
-1950	36.84	118.4	255.0	210.8	264.7	228.8
-2000	44.57	99.12	324.0	396.7	406.8	218.0

Clearly, the Q_A values increase with higher content of gallium in the alloy, as with the higher values of cathodic potential. The exception is Al-2.6 wt% Ga alloy, where the quantity of oxidized substance is considerably lower compared to the other alloys.

3.3. Cyclic voltammetry measurements

In Fig. 6, the cyclic voltammetry measurement results for 5N Al- 0.05wt% Ga, are given. Characteristic parameters and values of the cathodic Tafel plots for all alloys are shown in Table 3.

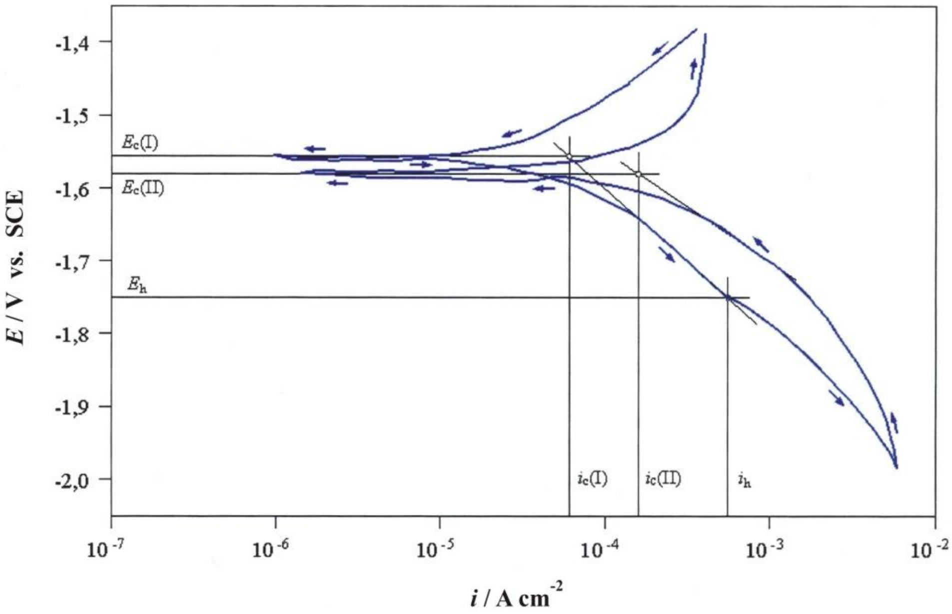


Figure 6 - Tafel plots for 5N Al - 0.05 wt% Ga alloy in 2M NaF solution at pH = 7

Table 3 - Characteristic parameters and values of the cathodic Tafel plots for all 5N Al - Ga alloys in 2M NaF solution

pH	E_c(I) (mV)	i_c(I) (μA cm^{-2}) Acm-22)	E_c(II) (mV)	i_c(II) (μA cm^{-2})	E_h (mV)	i_h(I) (μA cm^{-2}) Acm-22)
Al - 0,01% Ga						
1						
2						
3	-1365	6,9	-1450	1,2	-1560	31
4	-1600	120	-1550	57	-1680	400
5	-1615	135	-1540	78		
6	-1625	100	-1570	135		
7	-1640	80	-1615	47	-1755	800
8	-1680	82	-1615	110	-1810	840
9	-1680	125	-1585	140		
10	-1670	92	-1620	155		
Al - 0,02% Ga						
1						
2						
3	-1455	17	-1443	0,91	-1615	45
4	-1460	16	-1380	1,9	-1630	45
5	-1647	71	-1625	32,5		
6	-1600	230	-1560	68		
7	-1630	130	-1600	98		
8	-1685	81	-1660	99		
9	-1695	130	-1615	200		
10	-1710	125	-1665	100		

Al - 0,05% Ga						
1						
2						
3	-1470	27	-1330	1,8	-1565	46
4	-1395	83	-1485	2,4	-1895	580
5	-1475	120	-1520	4,4	-1870	450
6	-1490	62	-1655	19	-1795	400
7	-1565	60	-1580	165	-1760	560
8	-1575	47	-1735	37	-1880	500
9	-1590	47	-1725	71	-1770	360
10	-1570	110	-1750	80	-1775	260
Al - 0,1% Ga						
1						
2						
3	-1425	370	-1275	7,0	-1885	1100
4	-1458	13,5	-1440	2,6		
5	-1485	61	-1515	4,6	-1950	890
6	-1530	130	-1550	5,1	-1935	1400
7	-1600	140	-1570	240	-1790	1100
8	-1555	150	-1650	21	-1935	1100
9	-1635	160	-1665	14	-1975	1250
10	-1645	200	-1675	32	-1980	1750
Al - 0,2% Ga						
1						
2						
3	-1450	12,5	-1330	1,4	-1550	23
4	-1365	2,9	-1275	1,25	-1415	3,9
5	-1625	110	-1475	90		
6	-1430	76	-1490	30	-1875	1800
7	-1525	190	-1465	75	-1900	1700
8	-1520	160	-1550	13	-1900	1400
9	-1570	115	-1650	29	-1825	600
10	-1575	135	-1660	90	-1850	900
Al - 2,6% Ga						
1						
2						
3	-1370	42			-1570	81
4	-1370	1,75	-1560	7,5	-1520	13,5
5	-1505	170	-1680	110	-1905	2700
6	-1495	120	-1720	68	-1915	3100
7	-1600	1100	-1723	190	-1895	4900
8	-1600	310	-1725	120	-1855	1850
9	-1580	560	-1730	150	-1875	1850
10	-1470	700	-1705	100	-1870	1950

For Al-0.01 wt% Ga alloy, Table 3 shows that the hydration potential is determined for pH values 3; 4; 7 and 8. At all pH values (except for pH=3), E_c(II) is slightly more positive than E_c(I). A considerable dependence of E_c(I) and E_c(II) regarding the pH value (except for pH=3) has not been noted, which leads to a conclusion that the cathodic process has been carried out through oxide layer by the reduction of water molecules. For Al-0.02wt% Ga alloy, extremely negative values for E_c(I) and E_c(II) have been noted. The values for E_h can't be read from the voltammogram due to a slow, but constant current increase inside E_c(I) to - 2000 mV range; i. e. the current deviation does not occur from the Tafel direction. The Al - 0.05 wt% Ga and Al - 0.1 wt% Ga alloys show a slightly negative trend with the increase of pH values for E_c(I) and E_c(II). The hydration start point is shifted to highly negative potentials, as well. For Al-0.2 wt% Ga alloy, with the increase of pH values, E_c(I) and E_c(II) tend slightly negative (except for pH=3 and pH=4). Lastly, for Al - 2.6 wt% Ga alloy, highly negative values of E_c(II) indicate a possibility of a substance formation on an electrode surface that can be easily oxidized.

4. CONCLUSION

It has been experimentally confirmed that with adding of a relatively small amount of gallium to, in this case, high-purity aluminum, in contact with 2 M NaF solution, certain changes occur in basic metal behavior during cathodic polarization. Through the analysis conducted for the obtained measuring parameters, it has been established that the oxide layer keeps its properties in LCP range, while in HCP range a cathodic layering takes place, as well as the oxide hydration.

The measurements were conducted using the cyclic voltammetry method at low potential rate of $0.5 mVs^{-1}$ with the ability of stationary state simulation at every potential. Current-time responses and potential deviations can be read from Tafel dependence plots for non-stationary state.

When the obtained results are compared to the results for the alloys analyzed in 2M NaCl solution [8], the conclusion arises that alloys analyzed have more positive starting corrosion potential E_c(I) than all the alloys analyzed in 2M NaF solution, probably because fluoride ions shift the corrosion potential in negative direction.

According to the obtained Q_c values for all Al-Ga alloys prepared with high-purity aluminum, in high cathodic potential range a superactivity phenomenon can be expected.

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IZVOD

SVOJSTVA Al - Ga LEGURE TOKOM KATODNE POLARIZACIJE U RASTVORU NaF

U ovom radu analizirana su elektrokemijska svojstva superčistog aluminija uz dodatak malih količina galija pri visokom katodnom potencijalu. Potencijal anode je praćen u vremenu, u cilju određivanja količine naboja potrebnog za oksidaciju nastalih supstanci. Odgovori anodnih potencijala su bilježeni u vremenu od 1 sekunde. Vremenski odgovori za katodni i anodni potencijal snimani su i prikazani karakterističnim dijagramima. Raspon niskih i visokih katodnih potencijala (LCP, HCP) definiran je za sve uzorke. U eksperimentalnom radu korištena je standardna elektrokemijska ćelija sa zasićenom kalomel elektrodom (SCE) uz protuelektrodu od platine. Otopina korištena u radu je 2 M NaF.

Ključne riječi: *Legura Al-Ga, katodna polarizacija, aktivacija aluminija, otopina NaF, potencijal hidratacije.*

Naučni rad

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