ISPITIVANJE KOROZIONIH I MEHANIČKIH OSOBINA ALUMINIJUMA I NJEGOVIH LEGURA DOBIJENIH RECIKLAŽOM

TESTING OF THE CORROSION AND MECHANICAL PROPERTIES OF ALUMINUM AND ITS ALLOYS OBTAINED BY RECYCLING

Silvana DIMITRIJEVIĆ*[1], Aleksandra IVANOVIĆ[1], Stevan DIMITRIJEVIĆ[2],
Srba MLADENOVIĆ[3], Uroš STAMENKOVIĆ[3]
[1] Mining and Metallurgy Institute Bor
[2] Innovation Centre of TMF Belgrade, University of Belgrade
[3] Technical Faculty in Bor, University of Belgrade, Belgrade

Reciklaža aluminijuma je poznat proces koji se masovno koristi od sredine XX veka. Ovaj postupak je ekonomski isplativ i manje je štetan za životnu sredinu od proizvodnje aluminijuma iz primarnih izvora. Dobijen aluminijum je praktično idenitčnih karakteristika kao i metal pre reciklaže, ukoliko je čistoća proizvoda identična. I pored toga, dobijanje legura aluminijuma ili aluminijuma visoke čistoće iz recikliranih metala sa identičnim karakteristikama je zahtevan proces, naročito ako se reciklaža radi iz različitih materijala sa različitim primesama. U radu su prikazani rezultati poređenja korozionih karakteristika i fizičkih osobina 3 legure aluminijuma serija 1000, 3000 i 4000. Za elektrohemijsku karakterizaciju korišćene su metode: potencijal otvorenog kola (POK), linearn polarizacioni otpor (LPO) i Tafelova ekstrapolacija. Karakterizacija fizičkih osobina izvršena je merenjem tvrdoće i električne provodljivosti legura. Dobijeni rezultati potvrđuju male razlike između karakteristika komercijalnih i legura dobijenih iz procesa reciklaže. Neke od recikliranih legura imaju bolje karakteristike zbog manjeg udela primesa ili veće koncentracije, unutar standardnom dozvoljenih granica, nekih legirajućih komponenti kao što je silicijum.

Ključne reči: *Aluminijum; legure; reciklaža; korozija*

Aluminum recycling is a well-known process that has been widely used since the mid-20th century. This process is cost-effective and less harmful to the environment than the production of aluminum from the primary sources. The obtained aluminum has practically identical characteristics as well as metal before recycling if the product purity is identical. Nevertheless, the obtaining of high purity aluminium or aluminum alloys from recycled metals with identical characteristics is a demanding process, especially if recycling is made of different materials with different impurities. The results of comparison the corrosion characteristics and physical properties of three aluminum alloys, series 1000, 3000 and 4000 are shown in this paper. For the electrochemical characterization, the following methods were used: the open circuit potential (OCP), linear polarization resistance (LPR) and Tafel extrapolation. Characterization of physical properties was done by measuring the hardness and electrical conductivity of the alloys. The obtained results confirm small differences between the characteristics of commercial and alloys obtained from the recycling process. Some of the recycled alloys have better characteristics due to a lower concentration of impurities or higher concentration, within the standard allowable limitsof some alloying components such as silicon.

Keywords: *aluminum, alloys, recycling, corrosion*

1 Introduction

Aluminum is different from other metals due to a low density, good plasticity, satisfactory mechanical strength, high thermal and electrical conductivity. Aluminum is non-toxic, non-magnetic and corrosion-resistant in many environments, and also cheaper than the other non-ferrous metals. For those reason properties, aluminum has been widely used in many branches of the modern technology [1-4].

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[*] Corresponding author: silvana.dimitrijevic@irmbor.co.rs

Aluminum is a highly reactive metal with high affinity for oxygen. Due to this, it is used in aluminothermic reactions where aluminum is a reducing agent, and is oxidized by oxides of other metals (usually the first two): Fe, Cu, Ni, Cr, Mn and others [5-6]. It should be added that the standard electrode potential of aluminum is very negative (far from the field of thermodynamic stability of water). For reaction:

$$Al \Leftrightarrow Al^{3+} + 3e^{-} \qquad (1)$$

amounts to -1,662 V or -1,699 V in the older and more recent literature, respectively [7, 3]. Aluminum is a highly resistant to most environments and a large number of different chemical agents. This resistance is a result of the inertia and protective character of the aluminum oxide film, formed on the metal surface.

Nowadays, aluminum and its alloys are used practically in all areas of modern technology. They have the significant applications in the aviation and automobile industries, rail and water transport, construction, mechanical engineering, electrical engineering, chemical industry, packaging industry and other wide range products. High purity aluminum is widely used in the new areas of modern technology: energy, semiconductor electronics, radio technique, etc. In addition, aluminum should be corrosion-resistant in many aggressive environments. In order to achieve the strength and other mechanical properties, aluminum is alloyed with other elements (silicon, copper, magnesium, zinc, manganese). Industrial alloys of aluminum usually contain at least two or three alloying metals [8-10].

Aluminum alloys, depending on the alloying elements and the condition of the products, are divided into series. A numerical marking system was adopted to mark using the four-letter Arabic numerals, the first one defining the series, according to the prevailing alloying elements. There are 8 series of Al alloys. Common and standardized aluminum alloy groups are shown below [10-11]:

1000 commercial clean aluminum; 2000 Aluminum-copper; 3000 Aluminum-Manganese; 4000 Aluminum-silicon; 5000 Aluminum-magnesium; 6000 Aluminum-magnesium-silicon; 7000 are basically Al-Zn-Mg alloys; and 8000 Al-Fe-Si.

Aluminum is at the second place, just behind steel as the most used metal in the world for production the metal products. Only 30% of total aluminum production is from recycling. The primary advantage of aluminum over the other metals in the recycling process is that aluminum can be recycled many times without changing the important characteristics. The fact that recycling does not change the properties of aluminum has suggested that the new aluminum products can be made of 100% recycled material. Also, the production of new products from recycled aluminum requires much less energy. Compared to the production of primary aluminum (ore bauxite), savings of up to 95% are possible.

Numerous products of different uses made of aluminum are discarded after the expiry date. Examples of aluminum products that have a limited shelf life and through which the recyclable waste aluminum waste can be collected are, for example, various components of electronic devices (hard disk enclosures, CD readers or CD cutters, automotive wheels, bicycle frames, cans, packaging of certain cosmetic products (deodorant, hairspray and similar products in spray) and many other products. Also, aluminum waste contains no traces of corrosion (rust), so the collection of aluminum waste is safe for the collector of secondary raw materials. It does not contain lead; the aluminum waste has no harmful effect on the environment, which means that the storage of aluminum waste does not require any additional costs for preparing the storage space of warehouse.

The process of aluminum recycling is carried out in three phases: preparation - crushing and separation, drying of waste and melting of waste.

2. Experimental

The aim of research in this paper was the recycling of aluminum from the secondary raw materials, obtaining aluminum, and five alloys of commercial quality (Al - 1200; AlMn1Mg1 - 3004, AlSi10 - 4045; AlTi10 - 800; AlSi1MgMn - 6082; AlMnSi0.5 - 6060). The results of comparison the corrosion characteristics and physical properties of pure aluminum (Al 1200) and two commercial quality alloys (3004 and 4045), obtained by recycling are presented in the paper.

1.1 Methods and apparatuses

Secondary aluminum, in the first stage of recycling was separated from the other metals (primarily iron), crushed and melted. Melting of the secondary aluminum and alloys were carried out in the Heraeus K 1150/2 (voltage 380 V, 5 KW power) furnace, and the graphite molds were used for casting ingots. The results of comparison the corrosion characteristics and physical properties for pure aluminum (Al 1200), and two alloys AlMn1Mg1 (3004) and AlSi10 (4045) are presented. After casting, the samples were homogenized by annealing in order to eliminate the internal stress. Homogenized annealing was performed in an electric resistance furnace with a chamber. Plastic processing was performed by rolling at a total deformation degree of 70%.

The chemical characterization of samples were done using the XRF method (Roentgen Thermo Scientific Nitona XL3t-900: Niton, Palomar, Model: Niton XL3t-900 Series) by the XRD method (model: EXPLORER: GNR Analytical Instruments Group, Novara, Italy). Tensile strength and elongation tests were performed on a universal testing machine by tightening, pressing and bending the type "Mohr + Federhaf + Losenhansen" - Manheim.

The followings were used for the electrochemical characterization methods: open circuit potential (OCP), linear polarization resistance (LPO) and Tafel extrapolation. The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for the computerized control. The working surface of these electrodes was 0.50 cm^2. Platinum sheet was used as a contra electrode. Potential of the working electrodes was measured relative to a saturated calomel reference electrode (SCE). A potentiostate/galvanostate/ZRA Interface 1000™ (Gamry Instruments Inc.) and software package Gamry Framework (Version 6.25) was used for the electrochemical experiments. A Gamry Echem Analyst software package for analyzing the electrochemical data was used for analysis the results and determining the corrosion parameters.

1.2 Results and discussion

Table 1 Chemical composition of Al 1200, Al 3004 and Al 3045 as well as the composition according to the standard.

Table 1 Chemical composition as well as the composition according to the standard

Elem.	Al rec.	Al 1200 (with rec. Al)	AlMn1Mg1 (with rec. Al)	AlMn1Mg1 3004	AlSi10 (with rec. Al)	AlSi10 4045
Zn	0.09	max. 0.1	0.036	max. 0.25	0.1	max. 0.1
Cu	0.05	max. 0.05	0.212	max.0.25		max.0.30
Fe	0.4		0.60	max. 0.7	0.46	max. 0.8
Mn	0.05	max. 0.05	1.35	1-1.5	0.05	max. 0.05
Mg			1.24	0.8-1.3	0.04	max. 0.05
Cr					0.20	
Al	99.06	min. 99	96.29	min. 95.55	89.20	min. 87.70
Si	0.35		0.26	max.0.3	9.89	9-11
Fe+Si	0.75	<1.0				
Ti		max. 0.05	0.005		0.05	
Ni			0.003		0.005	
Be		max. 0.003				
Pb			0.003		0.003	
Other		Individually: 0.05 Total: 0.15	Ti: 0.005 Ni: 0.003 Pb: 0.003 Total: 0.011	Individually: 0.05 Total: 0.15	Ti: 0.05 Ni: 0.005 Pb: 0.003 Total: 0.072	Individually: 0.05 Total: 0.15
Σ	100.00		100.00		100.00	

It can be concluded from Table 1, which shows the chemical composition of aluminum and its alloys obtained by recycling, the all obtained products of commercial quality.

Table 2 presents the mechanical properties of Al and the alloys obtained by recycling.

Table 2 The mechanical properties of Al and the alloys obtained by recycling

	Rm, N/mm^2	Rp$_{0.2}$ /mm^2	A, %	Hardness, HB
Al rec.	125	95	4.8	35
Al 1200	130	100	5.1	37
AlMn1Mg1 (with rec. Al)	189	56	13	43
AlMn1Mg1 3004	200	60	14	45
AlSi10 (with rec. Al)	115	59	2.0	75
AlSi10 4045	120	64	2.3	80

Using the LPR and Tafel method, the corrosive current density (j_{corr}) was determined from which the corrosion rate (CR) can be calculated in mm/year. The corrosion rate, as obtained by calculating (does not represent a directly obtained experimental result), and indicates the uniform corrosion of materials in the investigated environment, which is more or less idealization of the real state. The calculation is based on the Faraday law, where the corrosion current density of one year is taken. It should be emphasized that this is an approximation because it is j_{corr} changes over time. All electrochemical experiments were performed in the sodium sulfate (Na_2SO_4) solutions, concentrations of 0.50 mol/dm^3 + 1 ml conc. H_2SO_4 (pH=2.50).

Open circuit potential (OCP) was monitored for a period of 60 minutes. The LPR was measured at potentials of ± 20 mV (compared to the OCP) for all samples at a scan rate of 0.125 mV/s. The Tafel polarization curves were measured at potentials of ± 200 mV in relation to the OCP at a scan rate 1 mV/s.

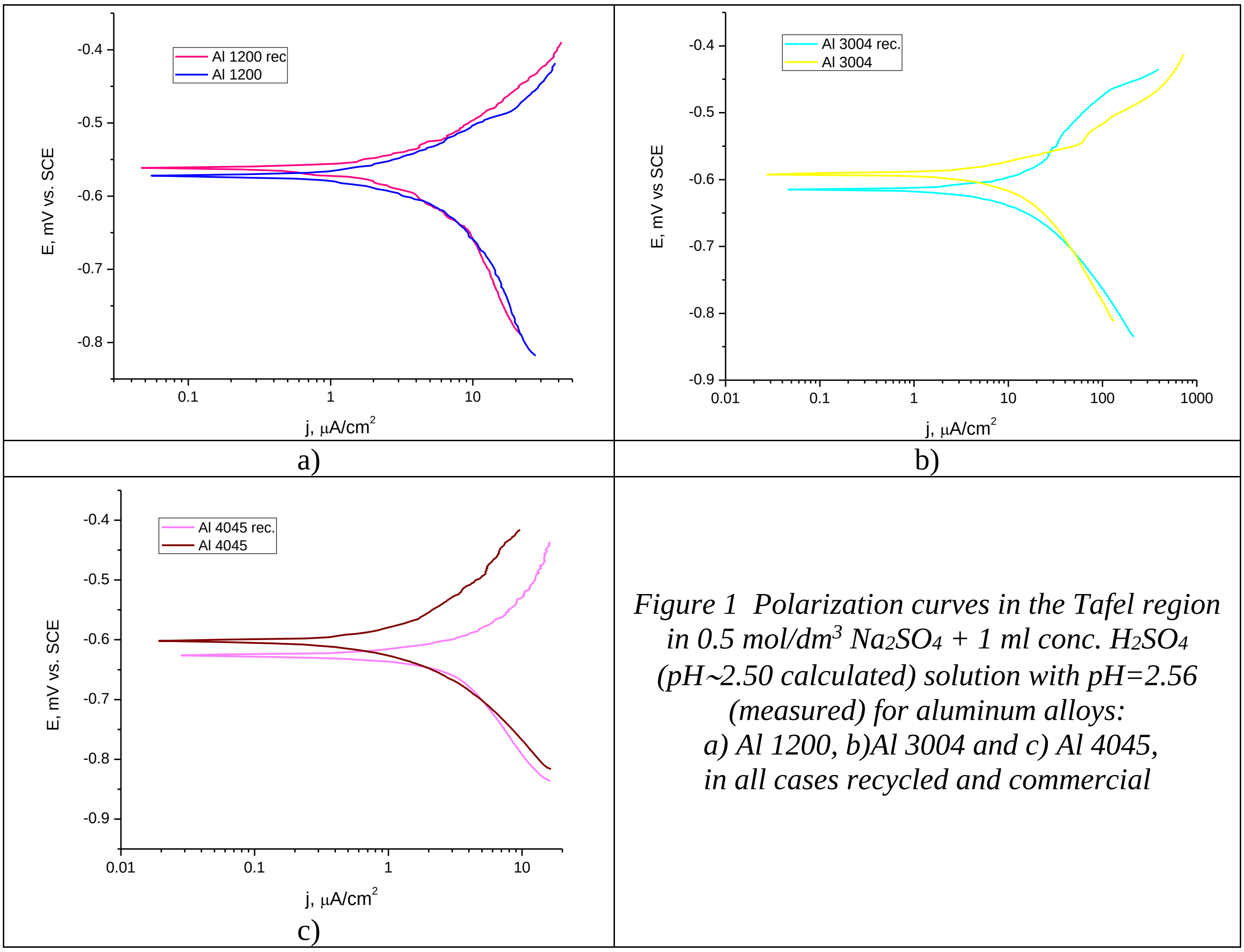
The results of the OCP and LPO measurements in the report are presented in Table 3, the first as the final (and relevant) value, and the other with all the results of analysis using the above software.

The results of electrochemical experiments are shown in Table 1 (OCP, Taffel's slopes, coefficients of the Stern-Geri equation (B). Polarization curves in the Tafel region for recycled and commercial alloys1200, 3004 and 4045 are shown in Figure 1 (a-c), respectively.

Table 3 Taffel's slopes, coefficients of the Stern-Geri equation (B) and OCP in 0.5M Na_2SO_4, pH=2.5 at 25°C for alloys with markings 1200, 3004 and 4045(recycled and commercial)

Alloys	β_a , mV/dec.	β_k , mV/dec.	B, mV	OCP, mV vs. SCE
Al 1200 rec.	89.1	–149.6	55.84	–562.6
Al 1200	94.8	–142.8	56.98	–572.2
Al 3004 rec.	89.7	–107.8	48.96	–615.4
Al 3004	81.5	–121.2	48.73	–593.8
Al 4045 rec.	107.6	–190.1	68.71	–624.9
Al 4045	130.8	–164.6	72.88	–603.2

Table 3 shows very similar values of Tafel slopes for the same alloy (obtained by recycling or not). The consequence is a great similarity between the parameter B (in mV) between recycled and commercial alloy in both cases (for alloy Al 3004 values are practically identical). In relation to them, for the Al 4045 alloy, it can be noted that the values of Tafel slopes are higher (approximately 120 mV/dec anodic and approximately 180 mV/dec. cathode) and, consequently the coefficient B has a slightly higher value. This does not indicate less corrosion resistance (directly) but more on a different corrosion mechanism in Tafel's area. The open circuit potential is similar to the 3004 alloy and slightly less negative (approximately 10 mV in both cases). Although this indicates less corrosion resistance, this is not certain due to a different corrosion mechanism, and later results show that this is a typical case that deviates from the rule.



a) b) c)

Figure 1 Polarization curves in the Tafel region in 0.5 mol/dm^3 Na$_2$SO$_4$ + 1 ml conc. H$_2$SO$_4$ (pH~2.50 calculated) solution with pH=2.56 (measured) for aluminum alloys: a) Al 1200, b)Al 3004 and c) Al 4045, in all cases recycled and commercial

It can be seen from Figure 1a (Tafel curves for alloy Al 1200 are shown), a slightly more positive corrosion potential in the recycled alloy. Shapes of curves are very similar and the value of corrosive current density for the commercial alloy (and the minimum value of j on graphics is slightly higher) is somewhat higher. The values for $j_{corr.}$ are slightly below 5 µA/cm^2.

For the Al 3004 alloys (Fig. 1b), a more positive corrosion potential for commercial alloy is noted. The difference is larger and easier to note than for the alloy 1200. The curves are still very similar, but with greater differences in the case of the alloy 3004. The figure indicates a somewhat lower but similar value of the corrosion current density for commercial alloy (and the minimum value of j on a graph is somewhat smaller). The values for $j_{corr.}$ are in the range between 5 and 10 µA/cm^2 for both alloys, which are higher than the alloy 1200.

Figure 1c (alloys Al 4045) shows a more positive corrosion potential for the commercial alloy (cca. 20 mV) confirming the results from Table 2. The curves for commercial and recycled alloys are very similar. The figure indicates that the cathode slope is higher for the recycled alloy, and for the anodic is the opposite, which is a detailed analysis and confirmed (Table 3). The figure shows the lower value of the corrosive current density for commercial alloy. It can also be observed that the anode current density at the end of measurement is lower for the commercial alloy, which also indicates its higher corrosion resistance in the measured environment. It is interesting that in a cathode direction of the current density at the beginning of the measurement (-200 mV in relation to the OCP) are almost identical for both alloys.

The values for corrosion potential and $j_{corr.}$ for the Tafel and LPR methods for all three alloys are given in Table 4.

Table 4 Corrosion parameters of alloys : Al 1200, Al 3004 and Al 4045 u 0,5M in 0.5M Na_2SO_4 + 1 ml conc. H_2SO_4 (pH=2.50), pH=2.5 at 25 °C for alloys with markings 1200, 3004 and 4045(recycled and commercial)

Alloys	Linear polarization			Tafel	
	Rp, kΩ/cm^2	Icorr., μA/cm^2	Ecorr. , mV vs. SCE	Icorr. , μA/cm^2	Ecorr. , mV vs. SCE
Al 1200 rec.	6,750	3,592	–560.6	3.28	–560.1
Al 1200	5,614	4,407	–569.5	3.65	–572.9
Al 3004 rec.	2,645	8,038	–613.7	7.88	–616.7
Al 3004	2,876	7,357	–594,6	7.34	–592.7
Al 4045 rec.	13.14	2,270	–625.5	**2,216**	–625.7
Al 4045	21.91	1,444	–601.6	**1,481**	–602.0

Table 4 confirms the indications in Figures 1a) and 1b), which means that the alloy 1200 (pure Al), obtained by recycling, it is slightly more resistant to corrosion in the investigated environment. The difference is somewhat higher for the LPO method, and is about 22%, while with the Tafel method it is only 11%. In both cases, there are slight differences in absolute terms, because only double value of corrosion current (or at least 50%) can be considered a really significant difference, especially since the differences themselves from 20% (and even more) are very common for identical tests of different research teams (as can be seen from the literature review).

It is an even better agreement between the LPO and Tafel's method in the case of alloy 3004. The obtained differences with these methods are almost identical. The recycled alloy, in contrast to the case, has a higher value of corrosion current density, and it was obtained by 9% and 7.5% more, in relation to the commercial, using the LPO and Tafel method, respectively. As both values are below 10%, it can be concluded that in the practical sense, the commercial alloy and recycled (Al 3004), are almost identical in terms of corrosion resistance in a slightly acidic sulfate environment. It should be noted that the values of corrosion potential for both methods and both alloys are very similar to those obtained by the OCP method. The differences from several mVs are negligible.

In the case of recycled alloy 4045, a higher corrosive current density is obtained by about 49% for the Tafel method and about 57% for the LPO method. The values of both methods for both types of alloys almost same (the difference is only a few percentages). This difference is significantly higher than for the alloys 1200 and 3004, but it is still in absolute amount relatively small, although it can be concluded that the commercial alloy is more resistant in the investigated corrosion environment. This can be explained by a slightly higher content of silicon in the commercial alloy (10.2% compared to 9.7%). It was probably that the burnt, during melting and casting, was inadequate (1.5%) and should be taken lower (1%). Additionally, this is due to the use of small batches where it is difficult to determine the ideal conditions for alloying, and where such small errors are common. However, it must be emphasized that the recycled alloy is entirely within the EN standard allowances (10 ± 1%).

Expectedly, the 4045 alloy showed better results than the alloys 1200 and 3004, which can be explained by the high concentration of silicon in the alloy that increases the corrosion. The obtained values $j_{corr.}$ are less than half that of the alloy 1200 and are almost five times less than for the alloy 3004. This can be considered a significant result, in the sense that it can be concluded that the alloy 4045 is much greater corrosion resistant in a slightly acid sulfate environment than the other two above. Also, it must be noted that the values of $j_{corr.}$ for all three alloys of the same order of magnitude, and the AlSi10 alloy is extremely resistant in the investigated corrosion environment. The conversion of the obtained results of corrosion rate of: 24.7 mm/year, and 15.8 mm/year for the recycled and commercial alloys 4045, respectively.

2 Conclusion

The results of testing this study show that the mechanical and corrosion properties of commercial alloys of aluminum and alloys obtained using the recycled aluminum does not significantly different. Better results for recycled alloys were for the alloy Al 1200. Commercial alloys with low density corrosion currents density were in the alloys 3004 and 4045. The largest difference was in the alloy 4045 where the recycled alloy had about 50% higher corrosion current. However, this is a relatively small difference in such measurements, and the result is a consequence of slightly lower content of silicon in the alloy. Since the main objective of the research was to compare commercial and recycled alloys, the results shown that the differences are small to insignificant and that the applied recycling process produces the alloys that are not only comparable, but often also slightly better than the commercial ones in terms of corrosion resistance. Since these alloys are generally not used in the solution itself, but only in the atmospheric conditions where sulfates are present, it can be concluded that the tested alloys can be successful used.

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