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Improvement of corrosion resistance of aluminium coatings at electric-arc sputtering with pulsating spraying flow

N.S. Kriuchkov, (Pryazovskyi state technical university) str. University 7, Mariupol, Ukraine. https://orcid.org/0000-0003-1012-0156
V.A. Royanov, (Pryazovskyi state technical university) str. University 7,
Mariupol, Ukraine. http://orcid.org/0000-0001-5379-9096
I.V. Zakharova, (Pryazovskyi state technical university) str. University 7, Mariupol, Ukraine.
http://orcid.org/ 0000-0002-3492-0134

Annotation: spraying technology is widely used to restore and strengthen worn parts of equipment in machine-building, metallurgical, mining, agricultural industries, which operate in abrasive, shock-abrasive, and gas-abrasive wear conditions and to which new and more stringent requirements are constantly applied.

Due to the increasing requirements for the quality and operational resistance of the restored surfaces of parts, the issues of improving the quality of coatings are very relevant for enterprises of various industries.

The major disadvantage of arc spraying is the process of oxidation of metal droplets during transportation to the processed surface, which has a significant impact on the quality of the coating and its operational characteristics.

Literature sources, in which by modern approaches the specific features of gas-air flow formation, different nozzle designs, combinations of mixtures and neutral gases are researched, reveal that the process of oxidation and burnout of alloying material is influenced by several factors, among which the structure of the spraying flow is the most significant. The authors proposed an arc spraying method using a pulsating spraying airflow.

Keywords: abrasive, impact-abrasive and gas-abrasive wear, alloying elements, non-metallic inclusions, pulsating flow.

Application of pulsating spraying flow at electric-arc sputtering was suggested at the department of Automation and mechanization of welding production of PSTU SHEI. The works [1,2] describe the method's principle as well as characteristics of the equipment, required for ensuring pulsations of the spraying flow, shapes and duration of impulses and flow's impact on sputtered metal.

Reduction of air oxygen impact upon liquid electrodes metal at electric-arc sputtering with pulsating sputtering flow was described in [5]. However, the results of investigations of the influence of pulsating sputtering flow upon corrosion resistance of aluminium coating are still missing.

The works [2,4] represent a positive impact of the spraying material and increase of the content of alloying components, like, for example, Mn, Si or C upon reduction of oxidizing level. Also noted were increase in the process productivity and efficiency of material application and the probability of lowering the oxide phase on particles' boundaries in the coating. The work [5] also contains the results of investigations of microhardness of coatings, sputtered at different frequencies of the pulsating flow.

The corrosion resistance of aluminium coatings was investigated on the specimens, obtained by means of electric-arc metallization with application of the pulsator, ensuring the pulsating frequency within 0-120Hz limit. Steel of Ст3 grade, in the form of plates 100 × 100 × 7mm in dimension was used as a base material. Prior to sputtering the specimens were degreased with solvent and underwent shot blasting treatment with subsequent blowdown with compressed air (with the objective of dust removing). Sputtering was performed by means of ЭМ-17 metallizator, equipped with the appliance of pulsating air supply, designed by the authors. AWS 5.10/5.10M : ER4043 wire was used. The chemical composition of the wire used was: Al – base, Si – 4.5-6.0, Fe – max. 0.6, Cu – max. 0.3, Mn – max. 0.05, Mg – max. 0.05, Zn – max. 0.1, Ti – max. 0.2, Be – max. 0.0003

Sputtering of wire 1.6mm in diameter was performed according to the following modes: air pressure 0.6 MPa, air consumption 2.5 m^3/min, arc current и 160-200 A, voltage 24-28V.

Sputtering at the optimal distance, equal to 170mm strictly at 90 degrees angle was carried out. In order to eliminate overheating of the coating sputtering was performed in a few stages. The layer about 0.5mm in thickness was sputtered with its subsequent cooling up to the ambient temperature. The overall coating thickness was about 3mm. After sputtering the deposited coating was removed from the base with application of a special tool. After that a specimen was cut from thus obtained part, 27x20mm in dimension, its total area was 0.00108 m^2 and its thickness was about 3mm.

Fig.1 The general view of the sputtered coating at 4x magnification

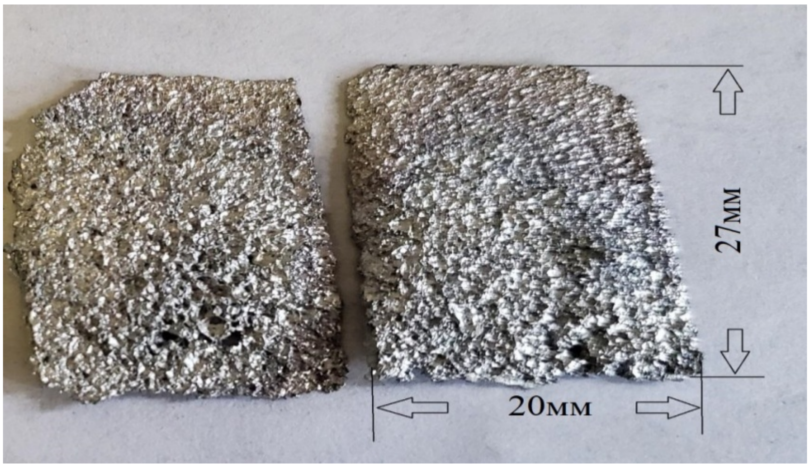

Fig.2 Specimens cut from the general coating After the specimens manufacturing they were put into special glass containers (see Fig.3) with addition of nitric acid HNO_3 for the first test and NaOH alkali

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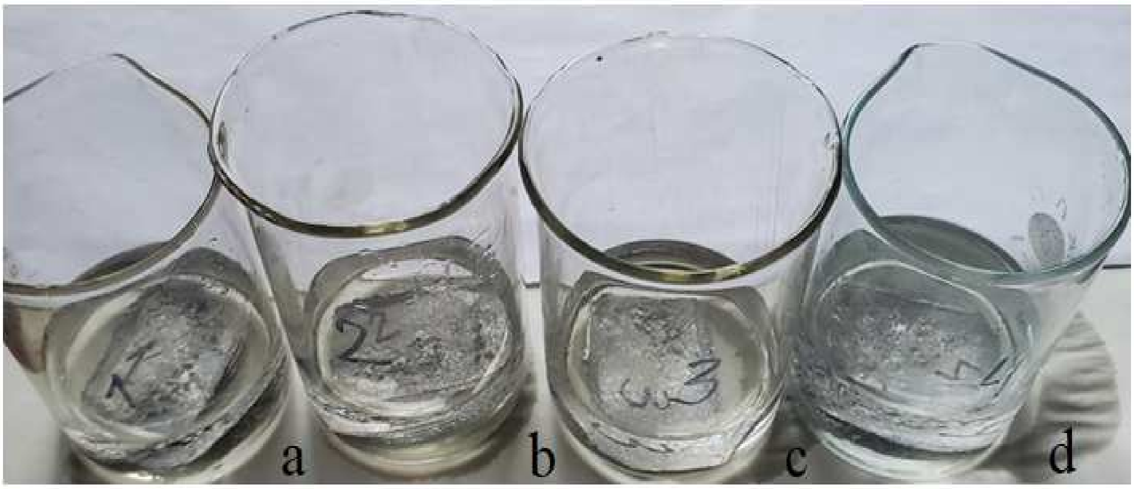

Fig. 3 Aluminium specimens in acid medium a-0Hz, b-20Hz, c-40Hz, d-60Hz

Aluminium is covered with protective oxide skin and retain high corrosion resistance both in water and in air. According to Pourbet's diagram [6] aluminium undergoes corrosion in acid media at pH < 2 and strong alkaline media with pH > 12, so it was decided to perform testing with application of an accelerated method, rather than a natural (in the open air) one.

Below we are going to present a calculation of the amount of oxygen, required for oxidation of 1 gram of aluminium. Now, let us compile an equation

$$4Al+3O_2 = 2Al_2O_3+Q \quad (1)$$

Where *Al* –aluminium, its weight according to the Periodic table being 26.981

O_2 –oxygen, its weight according to the periodic table is 16

$$26.981 \cdot 4 - 32 \cdot 3$$

$$1 - X$$

$$X= \frac{32 \cdot 3}{26.981 \cdot 4} = \frac{96}{107.92} = 0.889$$

It can be seen form these calculations that for oxidation reaction of 1g of aluminium it takes 0.889g of oxygen.

We also evaluate the amount of aluminium oxide formed after the reaction:

$$4Al+3O_2 = 2Al_2O_3+Q \quad (2)$$

$$26.981 \cdot 4 - [(26.981 \cdot 2) + (16 \cdot 3)] \cdot 2$$

$$1 - X$$

$$X= \frac{203.924}{107.924} = 1.88$$

It follows that after reaction with oxygen of 1 gram of aluminium 1.8g of oxide will be formed. Influence of reduction of oxygen content in the sputtering flow at electric-arc metallization was investigated.

Oxygen mass from the general flow for 10 seconds at different positions of pulsator's valve (k) is determined from the following equation:

$$m_{ki} = \frac{G \cdot p \cdot T \cdot (1-k)}{n} a_{O_2} \gamma_{O_2} \tag{3}$$

where G – is general air consumption, m^3 / min.

p – period of opening of pulsator's channel from the total cycle,%

n – frequency of pulsations, 1 /sec.

κ- the level of pulsator's channel opening,%

The obtained results help us build up the diagram of oxygen mass with regard to valve's positions.

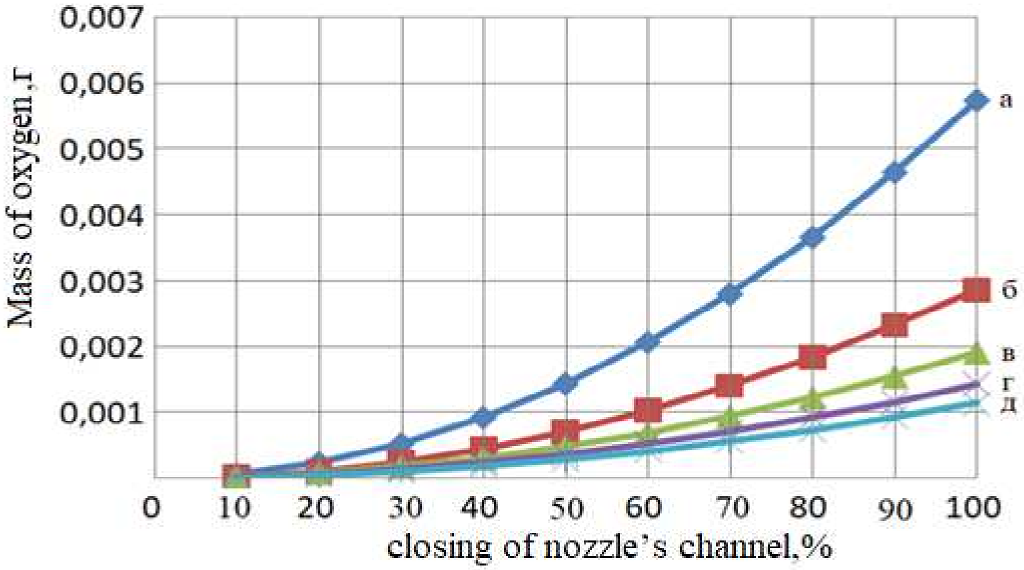

Fig.4 Mass of oxygen, passing through the nozzle's channel in 10n seconds at pulsating frequency а- 20 Hz, б- 40 Hz, в- 60 Hz, г- 80 Hz, д- 100 Hz

Reduction of oxide component of the coating, depending on the frequency of impulses of the sputtering flow can be easily seen on the photographs.

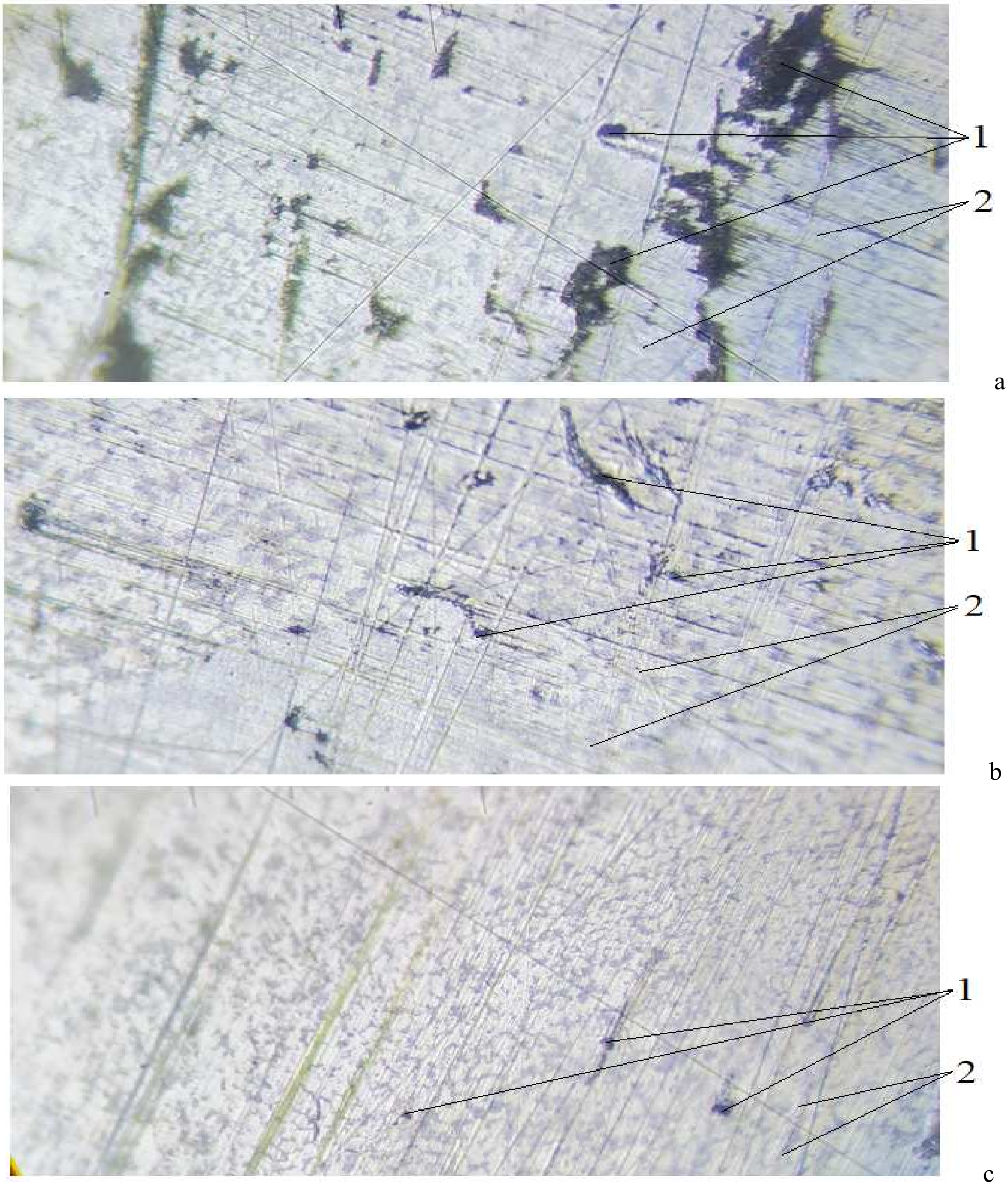

Fig. 5 Cross-section of Al coating, deposited at pulsation frequency (x400)
а- 0 Hz, б- 40 Hz, в- 80 Hz (1-oxides, 2-coating)

Reduction of O_2 with growth of frequency in the sputtering flow is obvious on the photographs.

Investigated was the influence of oxygen reduction in the sputtering flow upon corrosion resistance of the coating.

Dependence of aluminium corrosion rate upon pH medium, according to the data, obtained by the authors [6] is represented in Figure 5.

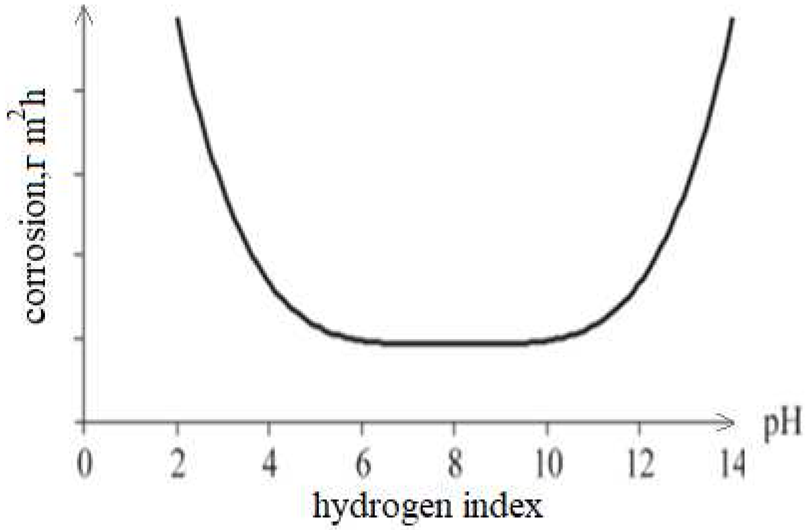

Fig.5 Dependence aluminium corrosion rate upon pH medium.

Aluminium corrodes in acid medium with oxygen and hydrogen depolarization. Corrosion was studied in 40% nitric acid.

On the anode:

$Al^0 - 3e = Al^{3+}$

On the cathode:

$O_2 + 2H^+ + 4e = 2OH^-$

Overall reactoin:

$4\ Al^0 + 3O_2 + 6\ H^+ = 4\ Al^{3+} + 6OH^-$

$4\ Al^0 + 3O_2 + 6\ HNO_3 = 2\ Al(OH)_3 + 2\ Al(NO_3)_3$

Intensive hydrogen release goes on alongside with this process on the cathode:

$2H^+ + 2e = H_2\uparrow$

A reaction with release of nitrous oxide is possible:

$8\ Al + 30\ HNO_3 = 8\ Al(NO_3)_3 + 3N_2O\uparrow + 15\ H_2O$

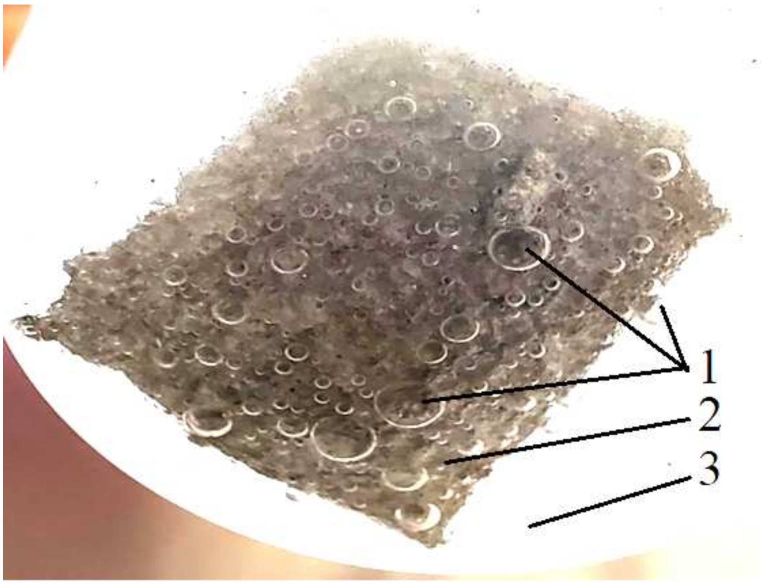

Fig.6 A specimen with active gassing in alkaline solution. 1- released gas, 2-coating, 3-solution

Aluminium hydroxide and aluminium nitride appear to be corrosion products. The obtained aluminium hydroxide can be represented as $Al_2O_3{\cdot}nH_2O$ forming protective oxide skin. The upper layers of thin nonporous oxide skin begin to loosen in the acid medium forming a porous oxide layer[7].

Corrosion rate of metals is characterized with mass losses in “g” per g/m^2 or corrosion depth “h” in mm/year. 12 ^0C Testing temperature 23 hours (reaction time)

Correlation between “g” and “h” values is determined by the formula [7]:

$$h = \frac{8760g}{\rho}, \quad (4)$$

where ρ – is metal of alloy density in kg/m^3.
The experiment’s data are represented in Table 1.

Table 1- Aluminium corrosion rate in nitric acid medium HNO_3

Coating frequency	Weight in g.; before	Weight in g.; after	Δ	Corrosion rate	
				mm/year	g/m^2 hour
0	0.982	0.840	0.142	18	5.72
20	0.792	0.670	0.122	16	4.91
40	1.042	0.933	0.109	14	4.38
60	0.806	0.710	0.096	12	3.86
80	0.845	0.761	0.084	11	3.38
100	0.943	0.868	0.075	9.7	3
Wire	3.506	3.479	0.027	1.42	0.44

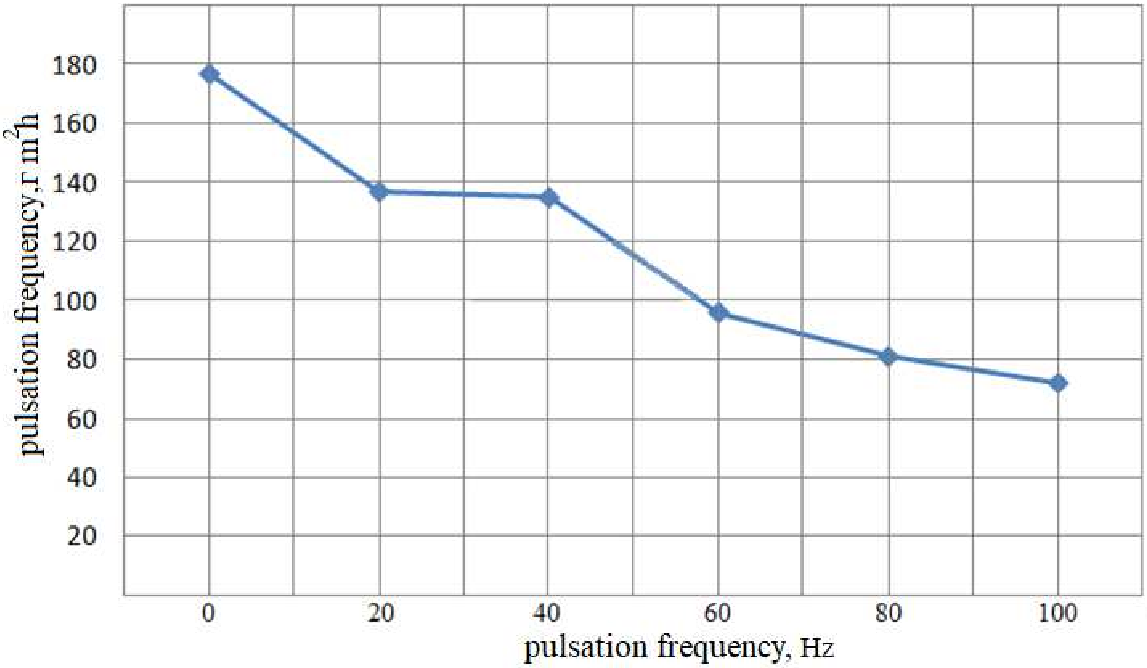

Figure 7 Al coating corrosion rate in HNO_3acid medium

It can be clearly seen in schedule 7 that there is reduction of corroding action with increase of the pulsating frequency of the sputtering flow. In the work [9] two mechanisms of corrosion cracking are analyzed: local anode solution and hydrogen embrittlement.

In case with local; anode solution on the surface of the part there are always some sections of unprotected metal (anode sections), their potential always being more negative that the potential of the sections, covered with oxide skin. So, intense aluminium oxidation happens to be on the anode sections. The resulting hydrogen is concentrated on the metal grain boundaries and on the sections of metal pitting destruction by oxygen, it causing hydrogen embrittlement.

Aluminium alkaline corrosion was investigated in 6% solution of sodium hydroxide, pH > 12.

Atmospheric properties of aluminium hydroxide determine its corrosion with hydrogen depolarization in alkaline solutions [5].

On the anode:

$Al^0 - 3e = Al^{3+}$

On the cathode:

$2H_2O + 2e = 2OH^- + H_2\uparrow$

The overall reaction:

$2Al^0 + 6H_2O = 2Al^{3+} + 6OH^- + 3H_2\uparrow$

or in a molecular view:

$2Al^0 + 6H_2O + 2NaOH = 2Na[Al(OH)_4] + 3H_2\uparrow$

It was noted that aluminium corrosion was quicker in alkaline medium as compared to acid medium with sufficient gassing.

After drying, the specimens that underwent corrosion both in acid and alkaline media possess clear black colouring.

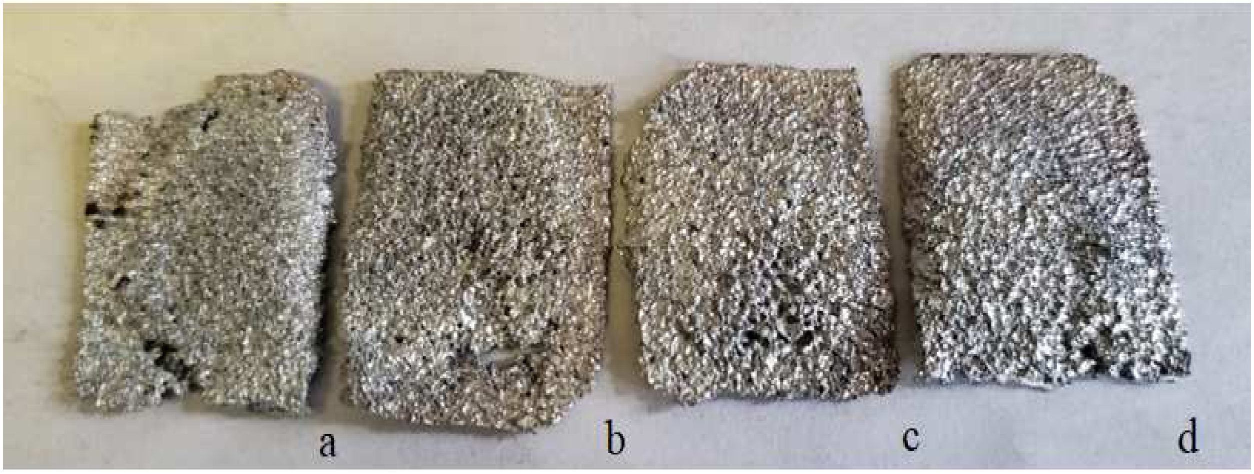

Fig.8 Aluminium specimens prior to testing
a-0Hz, b-20Hz, c-40Hz, d-60Hz

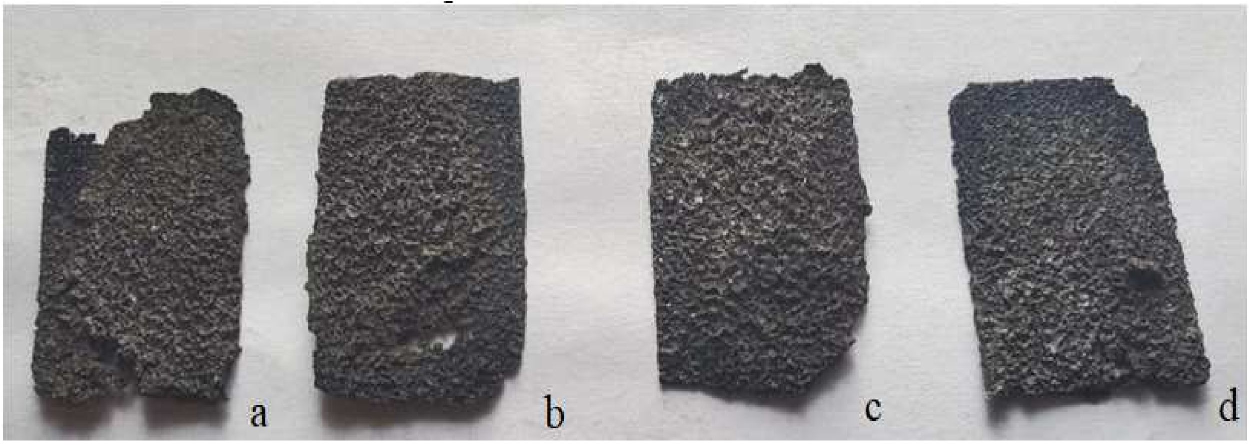

Fig. 9 Aluminium specimens after testing
a-0Hz, b-20Hz, c-40Hz, d-60Hz

NaOH Alkali Ph 14, 12 ^{0}C Testing temperature, 30 minutes reaction time

Table 2 – Aluminium corrosion rate in NaOH alkaline medium

Sputtering frequency	weight, g before	Weight, g after	Δ	Corrosion rate	
				mm/year	g/m^2 hour
0	0.662	0.566	96	573	177
20	0.760	0.686	74	443	137
40	0.612	0.539	73	437	135
60	0.1434	1.382	52	311	96
80	0.938	0.894	44	262	81
100	0.681	0.642	39	233	72
wire	3.507	3.474	33	81	25

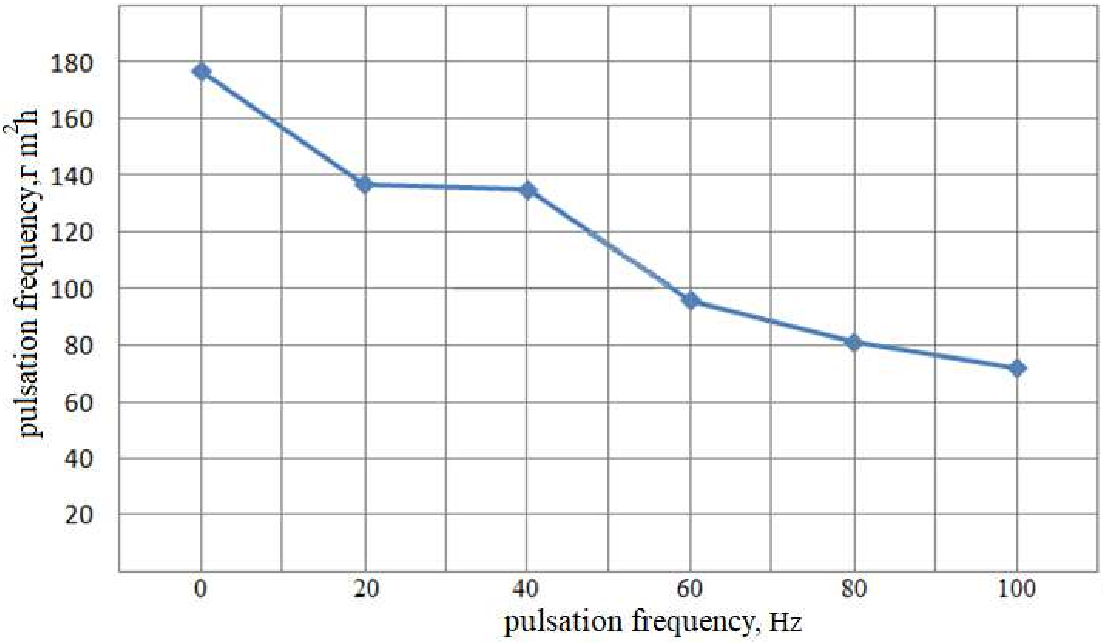

Fig. 10 Corrosion rate of Al coating in NaOH alkaline medium

Conclusions

1. It can be easily seen from the performed research that the pulsating frequency of the air flow has a direct influence on aluminium corrosion resistance. In acid medium corrosion resistance is increased by 52.5% and in alkaline by 40%.
2. It can be seen from the obtained data that aluminium corrosion proceeds 24-31 times faster in alkaline medium than in acid medium, depending on a specimen.

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