

CONTINUOUS SODIUM MODIFICATION OF NEARLY-EUTECTIC ALUMINIUM ALLOYS

K. Saja¹, A. Białobrzeski^{1,2}

Foundry Research Institute, Zakopiańska Str., 7330-418 Kraków, Poland¹
University of Bielsko-Biała, Willowa Str. 2, 43-309 Bielsko-Biała, Poland²

Abstract:

One of the possible techniques of continuous sodium modification of nearly-eutectic alloys is continuous electrolysis of sodium compounds (salts), taking place directly in metal bath (in crucible). For this process it is necessary to use a solid electrolyte conducting sodium ions. The main properties and methods to obtain solid electrolyte of „beta alumina” were highlighted, along with the possibilities of its application in foundry metallurgical processes.

KEYWORDS: MODIFICATION, CONTINUOUS MODIFICATION, BETA-ALUMINA

1. Introduction

The modification process of nearly-eutectic aluminium alloys is one of the most important operations in a melting process, since it not only affects the structure but also improves the mechanical properties of alloys, as evidenced by numerous references in technical literature [1,2,3].

One of the best modification processes applied to hypo- and nearly-eutectic aluminium alloys is that using metallic sodium introduced to the metal bath in crucible. Unfortunately, direct introduction of the addition of metallic sodium involves a rather violent course of the process. Additionally, some problems are faced with adequate sodium concentration maintained in the alloy, since with the time elapsing sodium tends to burn off [1,2,3].

Therefore, knowing these difficulties, it has been decided to look for other techniques by which sodium could be introduced into metal bath. Studies were oriented at the application of solid electrolyte of beta-alumina type introduced in the process of continuous modification to the hypo- and nearly-eutectic aluminium-silicon alloys with sodium compounds (salt) serving as a carrier for sodium ions. Studies were carried out at the Foundry Research Institute in Cracow within the framework of an open doctoral procedure at the Faculty of Processing, Materials Engineering and Applied Physics – Chair of Foundry Engineering, Czestochowa University of Technology, under the guidance of Promoter Prof. Andrzej Białobrzeski, DSc, PhD.

For such a process it is necessary to use solid electrolyte conducting sodium ions (ionic conductivity) and, at the same time, preserving the solid state of aggregation at the temperature of aluminium alloy melting and overheating, i.e. 660-750°C. Proper sodium salt of a melting point lower than the temperature of the liquid alloy, placed in a retort made of solid electrolyte, will undergo electrolysis as a result of the applied DC voltage. The retort is immersed in the melt. Anode is, liquid at this temperature, sodium salt connected with a DC source through e.g. a graphite electrode, and cathode is liquid aluminium alloy. Sodium ions, formed as a result of dissociation and electrolysis of sodium salt, are transported through the walls of solid electrolyte (material of the retort) and, in contact with the liquid alloy acting as a cathode, passing into atomic state, modify the metal bath. The surface area of the solid electrolyte (retort) contacting the liquid alloy is determined by the technological parameters of the process and controlled by changing the depth of the retort immersion in liquid alloy and / or by changing its diameter which, combined with the possibility to adjust the current values during electrolysis of the molten salt, allows for process control and obtaining the required sodium concentration in melt, necessary for alloy modification.

It can therefore be assumed that, in parallel with the loss of sodium in the melt, its content will be made up with an appropriate batch of modifier resulting from the electrolysis of sodium salt in a retort, which means that a balance of sodium content in the melt will be achieved and kept at a desired level [4,5]. Figure 1 shows a schematic representation of the continuous method of modification of aluminium alloys with sodium.

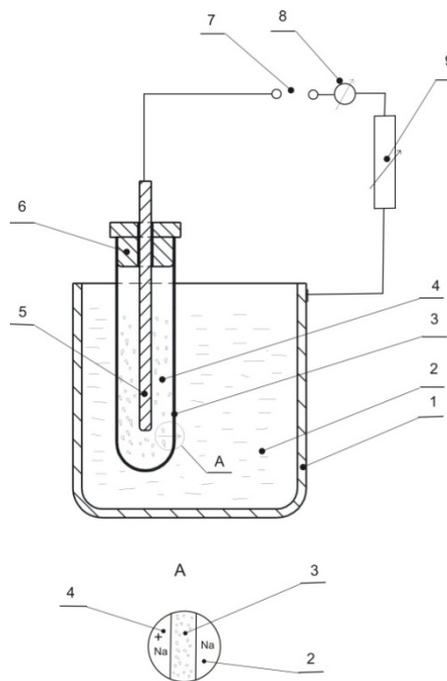


Fig. 1. Schematic representation of the continuous method of modification of aluminium alloys with sodium

1. crucible,
2. molten alloy (cathode),
3. retort made from solid electrolyte (anode),
4. molten sodium salt,
5. electrode, e.g. graphite,
6. porous plug stabilising the position of graphite electrode,
7. DC source,
8. meter,
9. resistor for current control in the circuit.

One of the few manufacturers of the ceramic materials which can be used as solid electrolytes, meeting also the technological requirements of an evolving process, is in the European market a British company IONOTEC LTD.

By suggestion of this Company, for operation in liquid aluminium alloy, more useful seem to be the, closed on one end, tubes (retorts) made of "beta-alumina" stabilised with zirconium (containing about 6% ZrO₂), which are good conductors for sodium ions. Zirconium, in this case, increases the resistance of the ceramic material to thermal shocks, which are inevitable under the conditions of the planned experiment, and also slightly reduce the ionic conductivity. Table 1 gives examples of the dimensions of produced tubes (retorts closed on one end).

Table 1. Examples of the dimensions of retorts made from beta-alumina according to IONOTEC specification [6]

Product designation	Length [mm]	Inner diameter [mm]	Wall thickness [mm]
A1	70	6,5	0,5-1,5
A2	105	13	0,5-1,5
H1	40	20	1-2
B1	100	30	1-2
B2	220	30	1-2
C2	220	55	2-3

When designing an experimental stand for continuous sodium modification of aluminium alloys, it was necessary to solve several technical problems related mainly with mounting of the solid electrolyte ("beta-alumina") retort filled with salt, and with voltage supply and protection of the terminal from the effect of molten alloy high temperature. To avoid the risk of short circuits between the voltage-feeding graphite electrode and "beta-alumina" retort, a ceramic insert was installed in the bottom of the retort and an electrode-insulating fabric in the upper part, as shown in Figure 2.



Fig.2. Retort closed on one end made from „beta alumina” with mounting elements used in the preliminary experiment

Figure 3 shows the mounting arrangement for a retort made of "beta-alumina". Electricity from an accumulator or from a thyristor power supply unit is fed through a graphite electrode, mounted on elements stabilising its position, to the interior of a retort filled with sodium salt. The retort itself is hung on a tripod with an insulator.



Fig. 3. The technique of mounting a retort made of "beta-alumina"

Allowing for guidelines given in the above description, a stand was designed and built in the Foundry Research Institute in Cracow for continuous sodium modification of hypo- and nearly-eutectic silumins; a general view of the stand is shown in Figure 4.



Fig. 4. General view of the experimental stand for continuous modification of aluminium alloys

2. Analysis of physico-chemical and ecological properties and selection of sodium salt for the process of electrolysis

It has been assumed that the material which is the source of sodium ions and which makes an anode in the process of electrolysis will be sodium salts of electrochemical and physical properties that meet the following criteria:

- **melting point** – the sodium salt must be liquid at the melting point of aluminium alloy to enable its dissociation and electrolysis (the melting point below 650°C);
- **boiling point** – it must be high enough to avoid salt evaporation at the operating temperature, as it can cause difficulties and excessive loss of salt;
- **reaction products of electrolysis** – the waste products of the salt electrolysis reaction should be low in volume and occur in the gaseous state. The solid state waste products can interfere with the reaction of electrolysis and contaminate the device;
- **safety aspects** - sodium must be safe in handling. Both the salt and its waste products must not be toxic;
- **economic aspects** – the selected salt should be cheap and readily available in the market.

The first salt that initially meets nearly all of the above mentioned requirements seems to be the table salt NaCl (iodine-free). However, this salt has a melting point of 801°C, i.e. higher than the melting temperature of aluminium alloys which is 670-730°C, and therefore the process of electrolysis is not possible. Other salts that meet the basic requirements can be e.g. sodium hexametaphosphate (NaPO₃)₆ with a melting point of 628°C, or sodium tripolyphosphate Na₅P₃O₁₀ with a melting point of 580°C. Another solution is to use mixtures of sodium salts, mainly chlorides, carbonates and sodium compounds with nitrogen. Based on the salt phase equilibrium diagrams, the molar or weight ratios of salts with a melting point lower than 650°C can be determined.

These salts are readily available in the market in the form of powder. After preparation of a salt mixture with predetermined ratios of components, the whole is melted and then re-ground. Thus prepared salt mixture can serve as a source of sodium supplied in the process of electrolysis conducted in a retort made from "beta-alumina" (solid electrolyte).

Allowing for the accepted criteria which the salt should satisfy, in the preliminary experiment, **sodium hexametaphosphate (NaPO₃)₆** was used. This is white crystalline and hygroscopic salt. Its **melting point is 628°C**, in terms of safety it is not hazardous, does not require special personal protective equipment, and the price is at approximately 50 PLN/kg.

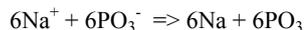
Preliminary calculations of the parameters of the salt electrolysis process (sodium hexametaphosphate (NaPO₃)₆) were carried out under the following assumptions:

- the amount of molten aluminium alloy (crucible capacity) - 20 kg;
- the process of alloy modification occurs with the sodium content at a level of 100 ppm;
- the current flowing in the system is approximately 10 A;
- the molar mass of sodium $M_{Na} = 22,989\,770$ [g / mole] [7].

Like its crystals, molten liquid sodium hexametaphosphate contains ions of Na⁺ and PO₃⁻, and for this reason when voltage is applied to the electrodes, the following processes can be expected to take place:

- cathodic reaction of $Na^+_{(c)} + e^- \Rightarrow Na_{(c)}$, which consists in sodium ion taking an electron supplied by the cathode, due to which this ion is transferred to atomic state;
- anodic reaction of $PO_3^- \Rightarrow PO_3 + e^-$, which consists in PO₃⁻ ions giving electrons to the anode (oxidation of ions), due to which these ions are transferred into the neutral atoms of PO₃.

The overall reaction is as follows:



As a result of the electrolysis of molten sodium hexametaphosphate, metallic sodium is produced on the cathode and the rest is PO₃.

According to Faraday's law of electrolysis, a relationship can be derived between the mass of products precipitated on the electrodes and the amount of electric charge consumed during electrolysis. Analysing the cathodic reaction of sodium, it is easy to notice that the supply of one mole of electrons gives one mole of sodium.

Using the Faraday constant [7] that defines the magnitude of electric charge per one mole of electrons, i.e.:

$$1 [F] = 96458,3399 [C/mol] = 1 [A] \cdot 1 [s]$$

we can calculate that the concentration of 100 ppm of sodium will be obtained when the electrolysis is conducted for 14 minutes under the conditions as mentioned above. Other values of the current intensity, electrolysis time and mass of the sodium supplied are shown in Figure 5.

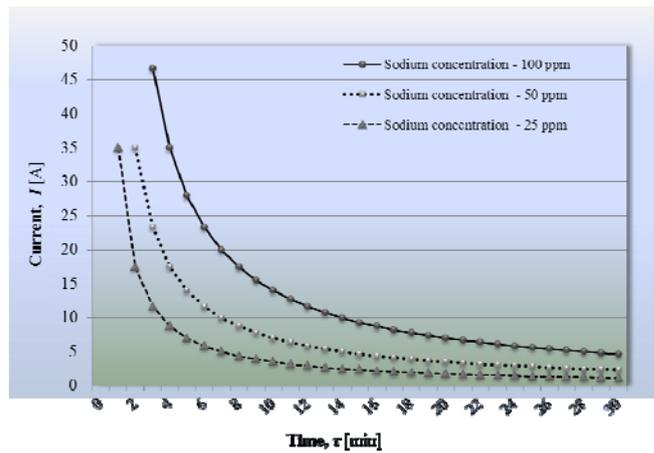


Fig. 5. The theoretical effect of time and current used in the electrolysis of sodium salts on sodium concentration in the alloy (own research)

3. Preliminary experiment with continuous modification of hypoeutectic aluminium alloys

After filling the retort with salt and assembly of the power supply system, for a few minutes the whole set was held over the surface of the AK7 alloy melt superheated to a temperature of 690°C to pre-heat the ceramic retort made of "beta-alumina" filled with the sodium salt to a temperature of about 300 -350°C, and reduce in this way the risk of its rupture when immersed in liquid alloy. Only then, the retort was slowly immersed in the alloy melt, as shown in Figure 6.



Fig. 6. View of the experimental stand

After immersing the retort made of "beta-alumina" in the liquid melt and closing the electric circuit, during the first 2-3 minutes the current was not flowing. This might be expected, because the sodium salt placed in the retort was not melted yet and the process of its dissociation and electrolysis could not be started. After about five minutes since the immersion of the retort, the ammeter showed the current value of 3.05 A, which indicated the beginning of electrolysis, that is, salt melting in the retort. After 10 minutes, the current was 11 A, and 15 minutes after the immersion of the retort in liquid alloy, the current value increased to 14.0 A. At this point, an alloy sample was cast (sample No. 4). After 25 minutes since the immersion of retort the current value was 12.4 A (sample No. 5), after 35 minutes the current was 12.5 A (sample No. 5), after 45 minutes the current intensity was 12.0 A (sample No. 6), after 55 minutes, the current was 11.0 A (sample No. 7), and after 65 minutes, the current was 9.0 A (sample No. 8).

Twenty five minutes after the start of the process, yellow flares appeared on the melt surface in the place where the retort material was in direct contact with the atmosphere. Probably it was sodium

burning out. This also proves the ongoing process of the diffusion of sodium ions through the solid electrolyte walls ("beta-alumina") to the volume of alloy melt. The drop of current suggested the decreasing amount of sodium ions, i.e. the decay of the process of electrolysis due to the depletion of salt in the retort. After 65 minutes, the first experimental process of the continuous aluminium alloy modification with sodium was stopped. The retort was carefully removed from the liquid alloy and cooled. No cracks were observed in the retort. This indicates a resistance of the ceramic material to thermal shocks. The retort was used in further experiments. Figure 7 shows the appearance of the retort after the experiment.



Fig. 7. The appearance of „beta alumina” retort after the completed experiment and removal from the metal melt

Samples 1 and 4-8 (including sample no. 1 of alloy in the starting condition) were examined for the sodium content. Table 2 summarises the conditions under which the experiment was carried out.

Table 2. Parameters and preliminary results of the experiment (AK7 alloy)

Sample No.	Time, τ , [min]	Current in the circuit, I , [A]	Sodium concentration in samples, C_p , [wt.%]	Notes: Alloy temperature maintained at 670°C
1	0	0	0,004	Starting sample
2	5	3,1	-	-
3	10	11,0	-	-
4	15	14,0	0,010	Sample taken for analysis
5	25	12,4	0,018	Sample taken for analysis
6	35	12,5	0,021	Sample taken for analysis
6	45	12,0	0,024	Sample taken for analysis
7	55	11,0	0,024	Sample taken for analysis
8	65	9,0	0,023	Sample taken for analysis

Figure 8 shows an increase of sodium concentration in the subsequent samples of AK7 alloy due to continuous sodium modification.

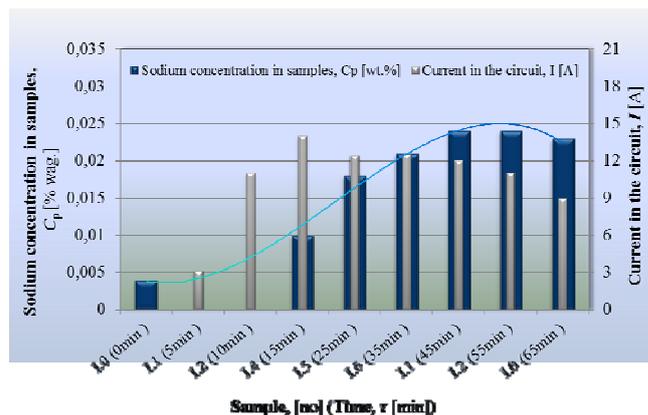


Fig. 8. Graphic representation of the process run

4. Conclusions

As a result of the preliminary experiment, it can be concluded that:

- under physico-chemical conditions typical of molten aluminium alloy, the solid "beta-alumina" electrolyte operates as a sodium ionic conductor;
- sodium concentration obtained in the melt even during the first preliminary experiment has clearly exceeded the concentration of this element necessary for the modification of aluminium alloys, thus creating a potentially wide range of the technological process parameters that can be selected for further use;
- sodium salt used in the initial experiment, i.e. sodium hexametaphosphate (NaPO_3)₆, has proved to be a salt of rather low efficiency, which means frequent refilling of the retort during the process of continuous modification. Therefore, in further research, the use of other sodium salts or of their mixtures will be considered;
- the conducted experiment is a good starting point for further advanced experimental research to evaluate the possibility to use continuous electrolysis of sodium salts for the modification of hypo- and nearly-eutectic aluminium alloys;
- the conducted studies expose the utilitarian nature of the work, which opens possibilities for an industrial application of the test results.

5. References

1. Wasilewski P.: Krzepnięcie Metali i Stopów: Siluminy – Modyfikacja i Jej Wpływ na Strukturę i Właściwości. PAN Bielsko Biała, Częstochowa, Opole 1993 ISSN 0208-9386
2. Fraś E.: Teoretyczne podstawy krystalizacji, część II. Skrypt AGH nr 1020 Kraków 1986
3. Flood S.C. Hunt J.D.: Modification of Al-Si eutectic alloys with Na. Metal Science 15/1981, July, s.287
4. A. Białobrzęski A.: „Continuous sodium modification of nearly-eutectic aluminium alloys. Part I. Theoretical backgrounds of the process”. Archives of Foundry Engineering Volume 7, Issue 1/2007, str. 53-56.
5. Białobrzęski A., Saja K., Leśniewski W.: „Continuous sodium modification of nearly-eutectic aluminium alloys. Part II. Experimental studies”. Archives of Foundry Engineering Volume 7, Issue 1/2007, str. 57-60.
6. <http://www.ionotec.com>
7. <http://www.chemicalelements.com>