ARCHIVES
of
FOUNDRY ENGINEERING

ISSN (1897-3310)
Volume 7
Issue 1/2007
57 – 60

11/1

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Continuous sodium modification of nearly-eutectic aluminium alloys. Part II. Experimental studiem

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Received 08.02.2007; Approved for print on: 12.03.2007

Abstract

One of the possible means of continuous sodium modification of nearly-eutectic alloys may be continuous electrolysis of sodium compounds (salts), taking place directly in metal bath (in the crucible). For this process it is necessary to use a solid electrolyte conducting sodium ions. Under the effect of the applied direct current voltage, sodium salt placed in a retort made from the solid electrolyte undergoes dissociation, and next - electrolysis. The retort is immersed in liquid metal. The anode is sodium salt, at that temperature occurring in liquid state, connected to the direct current source through, e.g. a graphite electrode, while cathode is the liquid metal. Sodium ions formed during the sodium salt dissociation and electrolysis are transported through the wall of the solid electrolyte (the material of the retort) and in contact with liquid alloy acting as a cathode, they are passing into atomic state, modifying the metal bath.

Keywords: modification, continuous modification

1. Physico-chemical backgrounds of the continuous process of Al-Si alloys modification with sodium

One of the means for continuous sodium modification (refining) of nearly-eutectic alloys may be continuous electrolysis of sodium compounds (salts), taking place directly in metal bath (in the crucible). For this process it is necessary to use a solid electrolyte conducting sodium ions (ionic conductance), which would, moreover, remain in solid state at the melting and overheating point of aluminium alloys, i.e. at 600-800 ^{o}C. Due to the applied direct current voltage, an appropriate sodium salt of a melting point lower than the temperature of liquid alloy, placed in e.g. a retort made from the solid electrolyte, will undergo an electrolysis. The retort is immersed in liquid metal. The anode is sodium salt, liquid at this temperature, connected to the source of direct current through e.g. a graphite electrode, while the cathode is liquid alloy. Sodium ions formed in the dissociation of sodium salt and electrolysis are transported through the wall of the solid electrolyte (the material of the retort), and in contact with liquid alloy acting as a cathode, they will be passing into atomic state, thus modifying the metal bath. The size of the solid electrolyte surface (the retort) contacting liquid alloy is dictated by the technological parameters of the process and is controlled by changing the depth of the retort immersion in liquid alloy and/or by changing its diameter which, combined with possible control of the current voltage during the process of molten salt electrolysis, should enable control of the process in terms of the best sodium concentration in metal bath necessary for alloy modification.

So, it can be assumed that, due to the electrolysis of sodium salt in retort, the loss of sodium in metal bath will be made up with proper batch of modifier, which will enable the state of equilibrium of the sodium content in alloy to be maintained at a required level.

Figure 1 shows basic assumptions of a new method of the continuous modification of aluminium alloys with sodium.

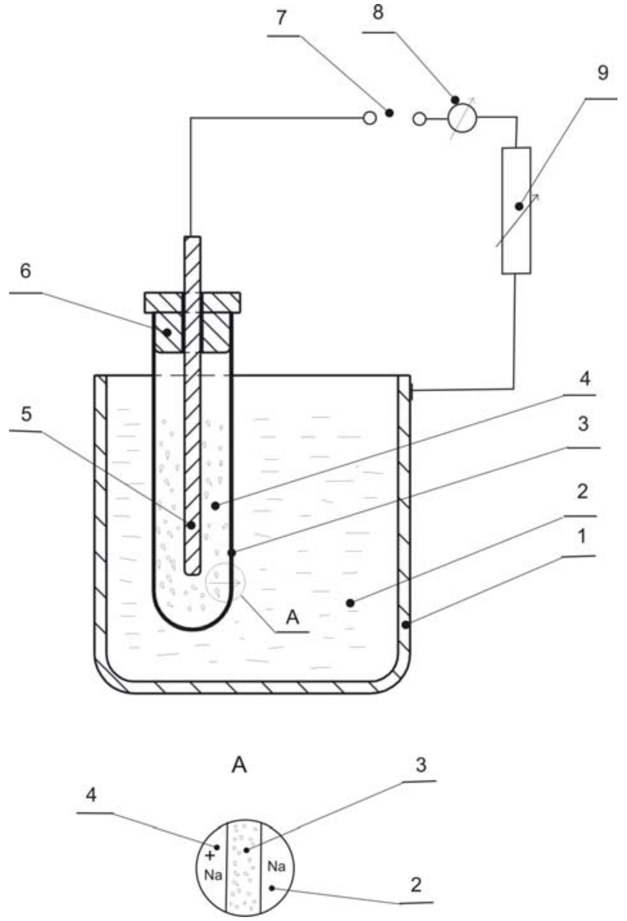

Fig. 1. Schematic representation of a new method of the continuous modification of aluminium alloys with sodium: 1. crucible, 2. liquid alloy, 3. retort made from solid electrolyte, 4..molten sodium salt, 5. electrode, e.g. made from graphite, 6. porous plug stabilising position of graphite electrode, 7.. source of direct current , 8..meter, 9..resistor for current control in circuit

2. Anode material - the source of sodium

The material which plays the role of anode during the process of electrolysis and which is supposed to be the source of sodium ions should, according to the preliminary assessments, offer the required electrochemical and physical properties, ensuring proper degree of safety in handling, availability, and acceptable price.

- Melting point. Sodium salt should be liquid at the melting point of aluminium alloy to enable its dissociation, followed by electrolysis (melting point below 650 ^{o}C),
- Boiling point should be high enough to prevent salt evaporation at the operating temperature, as it may cause some difficulties during work and excessive losses,
- Products of the reaction of electrolysis. The waste products of the salt electrolysis reaction should be kept at a low level and should occur mainly in gaseous state. If in solid state, their presence may hinder the reaction of electrolysis and contaminate the installation,
- Safety aspects. Sodium salt should be safe in handling. Both the salt and the waste must not by toxic.
- Economic aspects. The selected salt should be cheap and readily available on the market.

3. Experimental

At the Foundry Research Institute in Krakow, Poland, [1] experiments were conducted on the continuous modification of aluminium alloys with sodium. The method is the subject of patent submitted to the Patent Office. An objective of this experiment was finding out if the basic assumptions of the method were correct and if by the electrolysis of sodium salt in a retort made from the solid electrolyte it would be possible to increase the sodium concentration in alloy to a level necessary for its modification. The main tool used in this method was a readily available “beta-alumina” retort of 30 mm diameter and 220 mm length.

In construction of the pilot stand for trials of continuous sodium modification of aluminium alloys, a pictorial schematic representation of which is shown in Figure 1, it was necessary to solve a number of technical problems, i.e. fixing of the retort made from solid electrolyte ("beta-alumina") filled with salt, supplying the required voltage, and protecting thus obtained connection from the effect of high temperature of molten alloy. To protect the system from possible short-circuit between the graphite electrode supplying voltage and the retort made from "beta-alumina", a ceramic insert was placed on the bottom of the retort, and the electrode was in its upper part insulated with a cloth jacket, as shown in Figure 3. Figure 4 shows the system used for fixing of "beta-alumina" retort. The electric energy is supplied through graphite electrode to the inside of the retort filled with salt. The retort itself is mounted on a tripod with insulator.

Fig.3. “Beta alumina” retort blind-closed on one end, provided with fixing elements and ready for the experiment. Graphite electrode with elements stabilizing its location.

Preliminary parameters of the salt electrolysis process were calculated (the salt was sodium hexametaphosphate $(NaPO_3)_6$ adopting the following assumptions: amount of molten aluminium alloy (crucible capacity) - 10 kg, the process of alloy modification takes place with sodium content kept at a level of 100 ppm, current intensity in the system - about 10 A. From Faraday effect it follows that to pass the charge of the required value it will be necessary to conduct the electrolysis for about 420 seconds, i.e. for about 7 minutes.

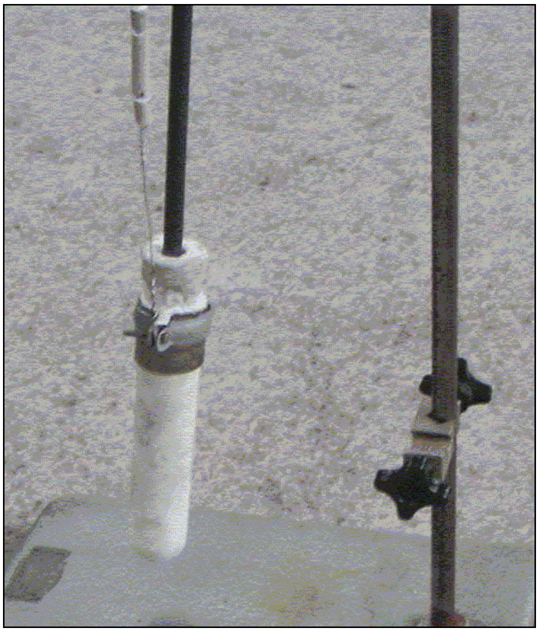

Fig. 4. The system for fixing a "beta-alumina" retort. The electric energy is supplied through graphite electrode to the inside of the retort filled with salt.

After filling of the retort with salt and connecting to the power system, the assembled set was held for over ten minutes directly above the AK7 alloy bath surface, overheated to a temperature of 670 ^{o}C, to preheat the ceramic retort of "beta-alumina" filled with sodium salt to a temperature of about 300-350 ^{o}C , reducing thus the risk of the retort failure in contact with liquid alloy. Only after this operation the retort was slowly immersed in liquid alloy, as shown in Figure 5.

Having immersed the retort of "beta-alumina" in liquid alloy and after closing of the electric circuit, the circuit remained dead for the first 2-3 minutes. It was just as expected, since sodium salt placed in the retort had not started to melt yet, and the process of its dissociation and electrolysis could not begin. After about 5 minutes since the moment of the retort being immersed, the ammeter showed the currect value at a level of 3,05 A, which indicated the beginning of the process of electrolysis, that is, melting of the salt in retort. After the lapse of 10 minutes, the value of the current raised to 11 A, after 15 minutes since the moment of immersing the electrode in liquid alloy the value of the current was 14,0 A. At this moment, a sample of the alloy was cast (sample no. 2). After 25 minutes since the moment of immersing the retort the value of the current was 12,4 A (sample no. 3), after 35 minutes the current was 12,5 A (sample no. 4), after 45 minutes it was 12,0 A (sample no. 5), after 55 minutes the current value was 11,0 A (sample no. 6), after 65 minutes the current value was 9,0 A.

Fig. 5. General view of the test stand. A retort made from "beta-alumina" immersed in liquid alloy.

After about 25 minutes of the process duration, on the surface of alloy melt, right in the spot where the retort material contacted the atmosphere, some yellow flashes were observed. This was most probably the effect of sodium burning out. This effect also proved that sodium ions were passing through the wall of the solid electrolyte ("beta-alumina") and were penetrating into the alloy.

A drop in the current value was suggesting the decreasing number of sodium ions, that is, the decay of the process of electrolysis due to the depletion of the salt volume in retort. After 65 minutes, the first test of the continuous modification of aluminium alloys with sodium was terminated. The retort was very carefully taken out from the bath and was cooled. No cracks were noted in the retort. This proves some resistance of the ceramic material to thermal shocks. The retort will be re-used in further experiments.

Samples nos. 1-7 (including sample no.1 which was the sample of base alloy) were examined for the sodium content. Table 1 states the conditions of the conducted experiment.

Figure 6 shows an increase in the concentration of sodium content in AK7 alloy in the successive samples due to a continuous modification of the alloy with sodium.

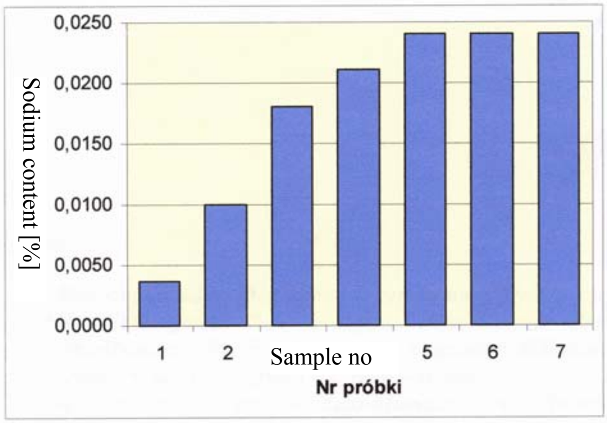

Fig. 6. Changes of sodium content in the successive samples of AK7 alloy (taken at 10 minute intervals) as a result of continuous modification

4. Conclusions

After analysis of the basic properties of various salts, for the preliminary trials it was decided to use as a sodium salt the sodium hexametaphosphate $(NaPO_3)_6$. This is a crystalline salt of white colour characterised by the melting point of 628 °C [7].

From the preliminary experiment the following conclusions were drawn:

- under the physico-chemical conditions typical of liquid aluminium alloy, the solid electrolyte of "beta-alumina" conducts sodium ions,
- the sodium concentration obtained in the aluminium alloy under the conditions of the first experiment considerably exceeded the levels necessary for modification of this alloy, which offers a wide range of the technological parameters to be chosen,
- the conducted experiment is a good starting point for more serious tests carried out on this process. Undertaking advanced research works on the theoretical and practical aspects of the process should finally result in application of this method in industrial practice.

Acknowledgments

The study was done under a research project no. 3 T08B 063 29

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