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Continuous modification of AK11 silumin with multicomponent salt on base of NaCl

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Abstract

Sodium belongs to the most effective modifying agents. The sodium can be brought into metal bath in metallic form or in form of chemical compounds comprising sodium, the most often in form of NaF. In the both above mentioned cases action of sodium is of very short duration, (what constitutes its main disadvantage), as lasting for about 15-20 minutes, mainly due to its evaporation from metal bath. Prolongation of modifying agent's action can be accomplished due to technology of continuous introduction of sodium to metal bath. That technology is based on continuous electrolysis of sodium salt, occurring directly in melting pot with liquid alloy. Application of solid electrolyte – conducting sodium ions (ionic conductance) – and simultaneously maintaining solid state of aggregation in melting and superheating temperature of alloy, i.e. 600÷800°C is indispensable for such process. Suitable sodium salt which is placed in retort produced from solid electrolyte shall undergo dissociation, and next electrolysis, in result of applied direct current. Sodium ions arisen during the dissociation of sodium salts and electrolysis are "conveyed" through retort walls made from solid electrolyte. In contact with liquid alloy as cathode, sodium ions pass to atomic state, modifying the alloy. The paper discusses results of initial study concerning process of continuous modification of AK11 silumin with use of multicomponent sodium salt on base of NaCl, shows results of tensile strength R_m and measurement of voltage drop for the alloy in solid state. Values of those parameters have confirmed obtained modification effect of investigated alloys. Assurance of stable run of continuous modification process brings about necessity of a further research aimed at optimization of parameters of the process.

Key words: Mechanical properties, Modification, Continuous modification, Electrolysis

1. Introduction

Silumins constitute the most widespread group among industrially employed cast aluminum alloys. These are technical alloys of aluminum with silicon as the main constituent in various configurations with other alloy additions. The alloys are broadly implemented in various branches of machinery industry. Such wide implementation results from their casting and utility properties. The alloys are characterized by low density, relatively low melting temperature, good thermal and electric conduction, good mechanical and casting properties (good castability, low shrinkage), good machinability and considerable corrosion resistance. Their susceptibility to formation of coarse-grained structure, having unfavorable effect on mechanical properties of alloys, is a pretty important defect from a technical point of view. [1]. Structure, strictly speaking its size, shape and way of distribution of hard and brittle crystals of silumin in plastic metallic matrix of solid solution α(Al) have significant effect on mechanical properties of silumins. In order to obtain suitable structure, and the same to have impact on properties of silumins, in practical applications one makes use of modification processes of those silumins [2]. Quality of structure modification depends on correct batching of modifying agent, temperature of metal and time elapsing from modification to solidification of the alloy [1-4].

Sodium can be a one from implemented modifying agents. Modification with sodium or its compounds is the oldest historically process of modification of silumins. That process, patented in 1920 by Pacz concerns hypoeutectic and approximately eutectic alloys only, whereas is not suitable for hypereutectic silumins, in which primary crystals of silicon are present in significant quantities.

In case of the modification consisting on adding sodium to metal bath, we deal with its transformation – in result of exchange reaction – from AlP to Na_3P. The Na_3P compound, not being a nucleus of crystallization for sodium, impacts on over-cooling of the bath and crystallization of eutectic mixture, leading to formation of fine-grained structure of the alloy [5].

Sodium is brought into metallic bath in metallic form or in form of chemical compounds comprising sodium. However, apart from a form in which the modifying agent is brought into metal bath its action is relatively short (about 15-20 minutes).

Permanent electrolysis of sodium compounds (salts) occurring directly in metal bath (in crucible) can be used as a method of continuous refinement (modification) of approximately eutectic alloys with sodium. To such process is necessary to use a solid electrolyte conducting ions of sodium (ionic conductivity) and simultaneously maintaining solid state of aggregation in melting and superheating temperature of alloy, i.e. 600÷800°C. Sodium salt, placed in container (retort) made from solid electrolyte, undergoes dissociation in result of applied direct current, and next electrolysis [4]. Liquid sodium salt connected with source of power supply through electrode, made from graphite or stainless steel, serves as anode. Liquid metal connected with power supply source by graphite electrode serves as cathode [5].

Sodium ions formed in result of dissociation and electrolysis are „conveyed" through walls of retort, and in result of contact with liquid alloy pass into atomic state, modifying the alloy.

Implementation of solid electrolyte, assuring ionic conductance and simultaneously maintaining solid state of aggregation in temperature of 600 – 800 ^{o}C, constitutes the basic condition to have the process running.

Stable, polycrystalline material on base of "beta-alumin", conducting sodium ions can serve as such electrolyte [6,7].

Primary ceramic material conducting ions of sodium (among others), accessible in form of thin-walled pipes (with different dimensions), bars, discs and plates is sodium „beta-alumin", produced with use of electrophoretic method, comprising 90-95% of β phase and about 0,5% of Na_2Al0_2, stabilized with lithium. There exists also a possibility to stabilize ceramics with magnesium or zirconium. Products manufactured on base of „beta-alumin" are durable polycrystalline ceramic materials, in which movable ions of Na, K, Ag, H, Pb, Sr and Ba can be implanted.

Material being source of sodium ions should have adequate electrochemical and physical properties, and should assure safe impact on environment [8,9].

2. Methodology of the research

Testing stand illustrated schematically in the Fig. 1 below was used to the testing.

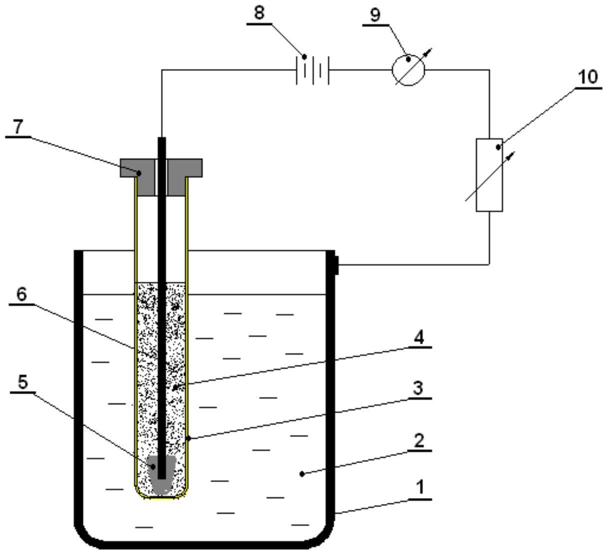

Fig 1. Scheme of the test stand:
1) melting pot, 2) liquid alloy, 3) retort, 4) sodium salt 5) ceramic insert, 6) electrode, 7) plug for stabilization of electrode's position 8) source of direct current, 9) measuring instrument, 10) resistor to adjust current in the circuit

Function of the electrolyte is performed by retort made from material on base of „beta-alumin". The retort, prior its usage, was stabilized (annealed) in temperature of 700 ^{o}C and cooled together with furnace.

In course of the experiments, as material of anode (source of sodium ions) there was used a salt comprising the following chemical compounds: NaCl, $NaNO_3$, Na_2CO_3.

Elements which directly ensure flow of the current are two electrodes – one immersed in liquid salt (anode), and the second one immersed in liquid alloy (cathode). In the Fig. 2 below is shown a view of the test stand with visible electrodes and retort.

Fig. 2. View of the test stand – retort and electrode (cathode) immersed in liquid alloy

After filling the retort with salt and after assembly of feeding system, the set was left for a few minutes directly underneath mirror of AK11 alloy overheated to temperature of 680 °C, in order to initial bringing-up ceramic retort made from „beta-alumin" and filled with salt to a temperature of about 300-350 °C, and the same to restrict possibility of crack of the retort in time of its immersion in liquid alloy. After immersing the retort filled with salt in liquid alloy, none actions were taken for a few minutes because the salt in retort was not melted completely. Electric circuit has been closed and current intensity was set to 5A as early as liquid state of the salt was obtained.

After immersing the retort with „beta-alumin" in liquid alloy and after closing the electric circuit, for the first few minutes electric current did not flow. It should be expected because sodium salt placed in the retort was not melted yet and process of its dissociation and electrolysis did not occurred yet.

Duration of the experiment was connected with quantity of melted material (melting pot capacity for 25 kg of alloy) from which the specimens were cast.

Specimens, which were successively cast during the whole duration of the experiment were marked in the Table 1 with an alphabetic letters. A given time when the specimen was cast (counting from beginning of the process) corresponds to each specimen. The first specimen marked with letter "R" has been cast 15 minutes after refining of the alloy. Successive specimens were cast during performed process of continuous modification of the alloy.. For each experiment there were cast three chill mould pieces used to test of voltage drop within given experiment, as well as to check the R_m tensile strength.

Measurements of voltage drop for specimens in solid state were performed with use of bench to measure conductivity in solid state (fig. 3). Measurement of voltage drop consists in applying two probes having suitable spacing to the specimen attached by fixing centers within closed circuit of flowing direct current, and read-out of voltage drop between electrodes with use of milivoltmeter. The measurement is performed several times for each specimen.

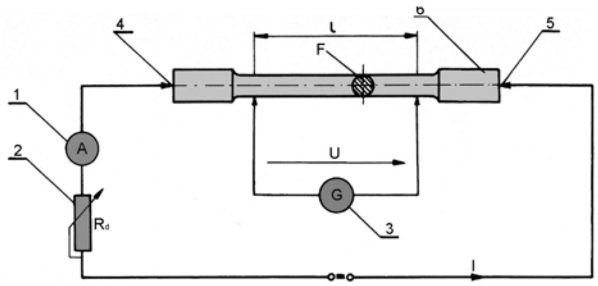

Fig. 3. Scheme of the stand to measurement of voltage drop: 1) ammeter, 2) decade rheostat, 3) galvanometer, 4, 5) terminals, 6) tested specimen, F) cross section of the specimen, U) drop of voltage on the specimen, l)- distance between measuring terminals

Measurement of voltage drop was carried out to determine correlation between its change and determined R_m tensile strength.

After termination of continuous modification process the retort was removed from liquid alloy and cooled down. None cracks were noticed. For instance, in the Fig. 4 is shown the retort after taking–off from metal bath.

Fig. 4. View of retort after removal from metal bath

3. Description of obtained results

In the Table 1 are shown conditions of performed experiment and obtained tensile strength R_m and voltage drop ΔU.

Table 1.
Conditions and results of the experiment

Specimen marked as	Duration of measurement [min]]	Intensity of current [A]]	Voltage drop ΔU [mV]	R_m [MPa]
R	15	0	0,48	210
A	5	5	0,486	221
B	15	5	0,452	250
C	30	5	0,419	247
D	60	5	0,423	246
E	90	5	0,419	250
F	120	5	0,417	246
G	150	4	0,402	241
H	180	3	0,405	247
I	210	1.5	0,41	239
J	240	0	0,412	231

The Fig. 5 shows change of tensile strength R_m during process of continuous modification of alloy.

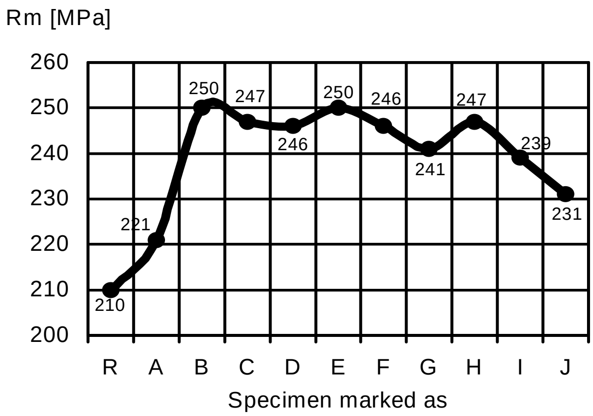

Fig. 5. Run of tensile strength change during modification of the alloy

Between refined specimens (R) and modified specimens there exists distinct difference in tensile strength R_m value. As early as 15 minutes after modification of alloy improvement of the mechanical properties Rm= 250 MPa can be seen. After 180 minutes there was observed a drop of mechanical properties resulted from loss of salt in retort.
Current intensity was maintained on constant level of 5A during 150min, whereas total time of modification process amounted to 240 min.

The drawing 6 shows voltage drop determined for the alloy in solid state during process of continuous modification of AK11 alloy.

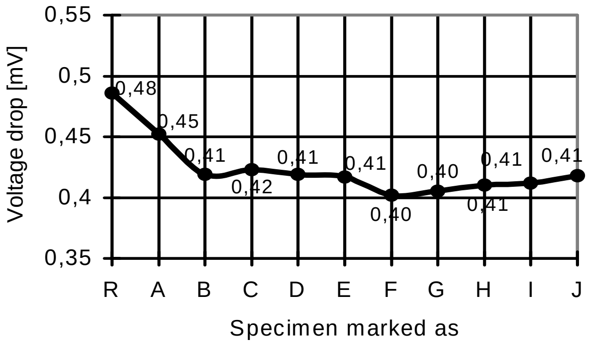

Fig. 6. Change of voltage drop during modification of the alloy

Measurement results of voltage drop performed in course of the process on cast specimens show at presence of correlation between change of structure of investigated silumin, being result of the modification, and values of ΔU obtained for the investigated alloy.

The equation (1) describes dependency between the voltage drop and R_m tensile strength of the investigated alloy.

$$R_m = 433,6 - 459,4\Delta U \quad (1)$$

R=0,85, R^2=0,73

4. Conclusions

Performed experiments have confirmed assumptions developed by professor Z. Lech – concerning taking advantage of physical-chemical properties of solid electrolytes (beta-alumin) in process of continuous modification of aluminum alloys with sodium

Obtained results of strength tests (R_m) have confirmed obtaining of the modification effect. That effect was maintained in continuous way during process of electrolyze of the salt. It points at conductivity of sodium ions through solid electrolyte in physical-chemical conditions present during melting and enriching (modification) processes of aluminum alloys.

There exists correlation between measured ΔU voltage drop and R_m tensile strength, what enables to use the method of voltage drop measurement to estimation of R_m tensile strength.

The method of voltage drop measurement can be used to quick check of modification results, obtained in the process of continuous modification of AK11 silumin

One from the most important issues connected with continuous modification of aluminum-silicon alloys is determination of suitable composition of salt, necessary to obtain required mechanical and physical properties.

Investigated salt complies with many criteria which are put on compounds discussed here, like long-lasting action among others, and connected with it cost reduction and simple chemical composition.

Continuous modification can constitute an answer of foundry industry to growing demand of optimization of processes, reduced quantities of scrap, improved productivity and repeatability of parameters of manufactured castings.

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