

Continuous sodium modification of nearly-eutectic aluminium alloys. Part I. Theoretical backgrounds of the process

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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

Aluminium alloys used most frequently in production of castings are silumins (Al-Si alloys) with nearly-eutectic content of silicon (about 12%) and with various other alloying additions. These alloys find application in different sectors of electro-engineering industry, like automotive sectors, precision engineering, aviation, household appliances, etc. The range of silumins application so wide is due to their very encouraging physico-chemical and technological properties. The alloys are characterised by relatively low density, low melting point, good thermal and electric conduction, and high mechanical properties (some silumins are heat treatable); in addition, they offer good casting properties (good castability and low shrinkage), good machinability and pretty high resistance to corrosion.

An important drawback of these alloys is their tendency to the formation of coarse-grained structure (this is mainly true in the

case of castings made in ceramic moulds and heavy-walled gravity die castings), which very obviously deteriorates the mechanical properties of the ready cast elements.

To modify (improve) this undesired structure, i.e. to refine it, some technological operations are recommended, consisting mainly in introducing to alloys very small amounts of some elements, which - being present at a level of about 0,01 % - cannot be treated as alloying additions. These are different metallic elements, called modifiers, like sodium, antimony, strontium, yttrium, etc. Using these elements, the alloy is subjected to the operation of modification, which will improve its mechanical properties.

Modification (from *Latin modyficare – to meter*) can be defined as a change introduced to any features of an object without changing its essence [9]. The process of modification is nothing new, as it has been used since the end of the 19th century, at first to improve the aluminium alloys. Nowadays, the operations of modification (using various techniques) are applicable to most of the commercial alloys.

The process of modification can cause in alloys,

depending on the type of alloy and of the modifier, a number of effects, e.g. formation of additional nuclei of crystallisation, formation of inclusions hindering the growth of crystals (the structure of alloys is of a polycrystalline nature), causing local changes in elements concentration and surface tension, changes in the conditions of alloy undercooling, deoxidising and degassing of the melt, etc. In view of the fact that modification may exert so multi-sided effects, no consistent and general theory of this process has been developed so far, while there are various hypotheses which try to describe the phenomena related with alloy modification.

The hypotheses can be divided into several groups:

- hypotheses of the confined crystal growth are related with changes in adsorption rate of the modifier present around the crystals in the form of a thin layer on the surface of the crystallisation nuclei, or with changes in surface tension at the crystal/liquid interface. These are numerous hypotheses interrelating the degree of structure refinement with surface effects, confirmed by the investigations conducted on different alloys,
- hypotheses of the formation of numerous heterogeneous nuclei of crystallisation, reducing the degree of undercooling for the start of nucleation, and hence generating an increased number of nuclei which cause refinement of the polycrystalline alloy structure. According to these hypotheses, the effect of modifier decreases with increasing alloy temperature and prolonged time during which the alloy is held in liquid state. Here, it is worth noting that in the case of silumins modification with e.g. sodium, the effect of constrained silicon nucleation is observed to take place, and it raises the degree of undercooling during eutectic crystallisation, and this, in turn, can be a measure of the modification effectiveness. Undercooling also occurs when alloy is cast in metal moulds, where the heat transfer rate from the solidifying casting to die occurs very rapidly. This is particularly well visible in the case of pressure die casting, where the effect of squeeze pressure makes the formation of a shrinkage air gap reducing the alloy cooling rate impossible. Therefore, in this case, it is not necessary to modify the cast alloy, as its rapid cooling promotes the formation of fine-grained structure.
- molecular -energy hypotheses (e.g. Ohno hypotheses),
- hypothesis distinguishing two groups of modifiers, i.e. modifiers soluble in alloy, which cause reduced surface tension with simultaneous adsorption of modifier on the surface of the crystallisation nuclei forming a buffer layer for further clustering of atoms in the liquid, thus reducing their growth, and into modifiers non-soluble, which act as heterogeneous nuclei, the more effective, the more their crystallographic lattice approaches the lattice of the modified alloy (isomorphism).

These hypotheses, or the groups of hypotheses, have been mentioned mainly because they describe the effects of modification as observed to take place in industrial practice. The number of these hypotheses is growing, as the new ones are emerging all the time. This proves how complicated the effects of alloy modification are and how important this process is for industrial practice [2, 6, 9].

One of the very few drawbacks of Al-Si alloys -

otherwise called silumins - is the eutectic structure which, with standard industrial quality of raw materials used in their production, is on a border of an anomalous, one might even say - degenerated, eutectic, caused by the formation of coarse-grained eutectic silicon. This is due to the presence in alloy of trace amounts of phosphorus which acts as a nucleation site for silicon crystallisation (AIP). The return to normal (fine-grained) eutectic is obtained by its modification, e.g. by adding sodium (in an amount of about 0,008-0,015 %) to the melt; which due to a reaction of exchange is transformed from AIP to Na₃P. The Na₃P compound is not acting as a nucleus of crystallisation for silicon, due to which the effect of bath undercooling and spontaneous crystallisation of eutectic take place, resulting in the formation of fine-grained and highly desired alloy structure.

Sodium is one of the most effective modifiers, introduced to metal bath either in metallic form, or in the form of chemical compounds, usually as NaP. In any of these cases, the effect of sodium is of a very short duration (and this is its main drawback). It lasts about 15-20 minutes, mainly because of the evaporation of sodium from the metal bath. After this time, the operation of alloy modification has to be repeated, which requires breaking of production cycle for some minutes. When castings are made in ceramic moulds, this break is of no major importance, since alloy modification may take place during the time when moulds are prepared for pouring, but when metal is poured into metal moulds (dies) and production is carried out in a continuous mode, a break like this cannot be accepted. Numerous attempts at finding other ways of alloy refining of longer duration, e.g. by using strontium (permanent modification used mainly in metallurgical processes of aluminium fabrication) are for many various reasons not applicable under the production conditions of foundries, and sodium continues being the best modifier of alloy structure in nearly eutectic Al-Si systems.

Sodium (Na) of atomic number 11 is included into the family of alkaline metals; in solidified condition it is characterised by a regular crystal lattice. Its melting point is 97,8 °C, while the evaporation point is 552,9 °C, which explains the effect of its rapid evaporation at the temperature of molten aluminium alloys (above 670 °C). At ambient temperature, the specific density of sodium is 0,971 g/cm³ [14].

One of the solutions for continuous modification (refining of nearly-eutectic alloys carried out with sodium) may be continuous electrolysis of sodium compounds (salts), taking place directly in metal bath (in crucible). This process requires the use of a solid electrolyte that would conduct sodium ions (ionic conductance) and would maintain the solid state of aggregation at the temperature of aluminium alloys melting and overheating, i.e. at 600-800 °C.

Practical possibility of using such process has been greatly enhanced by the synthesis of a ceramic material capable of conducting sodium ions at high temperatures. The first attempts at using „beta-alumina” in metallurgical industry were undertaken at a level of basic research in 1993 under a research project financed by EU. FOSECO became interested in this technology. The subject also raised interest of the academic and industrial centres in Great Britain and Belgium, best expressed in COSMA (Controlled Addition of Sodium Modifier to Aluminium Alloys) Project.

2. Ceramic material (solid electrolyte) - a derivative of alumina

At the beginning of past century, specially on account of vivid interest that production of aluminium raised in industry, studies were initiated on a raw material for its fabrication, viz. on alumina obtained from ore in Bayer process. Hydrated alumina occurs in several allotropic forms, like hydrargillite (gibbsite), boehmite, diaspore. The metallic ore composed in prevailing part of aluminium hydroxide is bauxite - the main source of metallic aluminium. To obtain pure aluminium, pure aluminium oxides with cryolite ($\text{Na}_3[\text{AlF}_6]$) acting as a flux are subjected to electrolysis.

Of great practical importance is natural alumina Al_2O_3 - corundum, obtained from bauxite (variation α and metastable variation γ). Corundum ($\alpha\text{-Al}_2\text{O}_3$) is a stable variation occurring under normal conditions in nature. It can be also obtained by roasting of diaspore. Trigonal corundum ($\alpha\text{-Al}_2\text{O}_3$) is composed of oxygen ions in dense hexagonal packing, where each ion of oxygen is surrounded by 4 ions of aluminium Al^{3+} .

A $\gamma\text{-Al}_2\text{O}_3$ variation is obtained by roasting of boehmite. This variation has the same type of crystallographic lattice as spinels. This form is unstable over the entire range of temperatures and does not occur under natural conditions. A regular variation of alumina is formed through dehydration of hydrargillite at a temperature of 900-950 °C, proper formula of this oxide being $\text{Al}_{21,5}\text{O}_{32}$, and so, this is not, as a matter of fact, Al_2O_3 . In $\gamma\text{-Al}_2\text{O}_3$ some sites in the crystallographic lattice assigned for aluminium are vacant.

Besides the above mentioned allotropic forms of alumina, the presence of alumina compound containing sodium ($\beta\text{-Al}_2\text{O}_3$) was also detected. The structure of the crystallographic lattice is loose, and sodium oxides (Na_2O) play the role of stabilizers - it is composed of spinel blocks between which there are atoms of sodium in an amount of 5-10%, which make it soft and easily spalling in thin lamellae. Acting on $\beta\text{-Al}_2\text{O}_3$ with molten salts of alkaline elements (BaCl_2 , SrCl_2 , CaCl_2), a reaction of exchange is proceeding with the formation of compounds, like $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$, $\text{SrO}\cdot 6\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$.

It is assumed that this is not an allotropic form of Al_2O_3 , but a different compound of the chemical composition $\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$ called "**beta-alumina**". More detailed investigations have proved that the compound may have an extended chemical composition, namely that of $11\text{Al}_2\text{O}_3 \cdot x\text{Na}_2\text{O}$, where the value of x is 1,25 - 1,4; after more advanced investigations this value was rated at $x = 1,0 - 1,6$. Even then it was observed that the material in solid state conducts electric current very well, and its electric conductivity raises with increase of temperature, assuming high values at the aluminium alloys melting point. The main material is sodium "beta-alumina" obtained by electrophoresis and containing 90-95% of beta phase and 0,5% of Na_2AlO_2 stabilised with lithium. It is possible to stabilise also the ceramic material with magnesium or zirconium to improve its resistance to thermal shocks.

The high ionic conductance is a result of high mobility of sodium ions, which in the structure of beta-alumina occupy the positions in planes separating two or three (depending on the

phase type) spinel blocks composed of the four, densely packed, layers of oxide ions, where ions Al^{3+} assume partly octahedric and partly tetrahedric position, as shown in Figure 1.

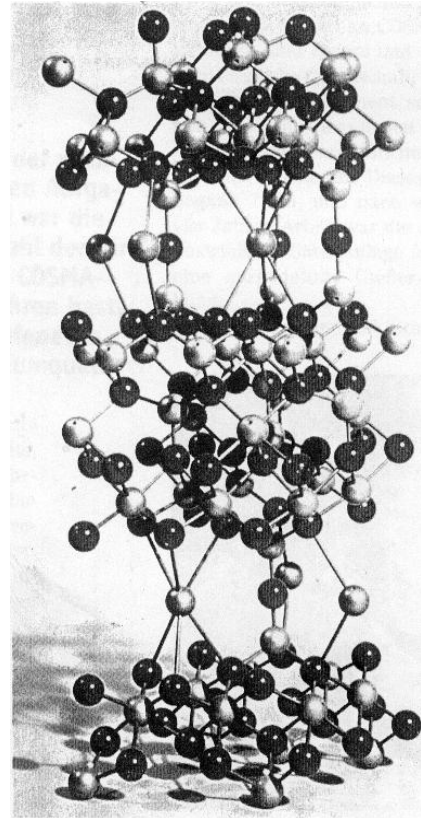


Fig. 1. The structure of beta-alumina

The laminar structure of material is, in principle, characterised by high anisotropy of both mechanical and electric properties. It is possible to produce a material of more homogeneous (isotropic) properties, shaping ceramic elements from fine-grained powder. The method consists in depositing beta-alumina powder on an electrode of specially designed configuration under the effect of voltage applied to this electrode while it is immersed in suspension formed by powder dispersed in liquid. The effectiveness of electrophoresis depends on the powder capability of capturing electric charges from the liquid in which it has been dispersed. The liquid may be e.g. n-amyl alcohol $\text{C}_5\text{H}_{11}\text{OH}$ [4]. The kinetics of electrophoresis depends on the following factors: suspension concentration, electric charge acquired by the particles in suspension, the value of voltage applied to electrodes, and the type of liquid acting as a dispersing phase (its dielectric constant and absolute viscosity).

The method of electrophoresis was for the first time used by J. M. Andrews to fabricate shaped elements from beta-alumina [11], the next one to use it was Y. Lazanec [12] who combined this method with isostatic pressing of shaped elements. I. H. Kennedy [13] made trials of direct roasting of beta-alumina shapes fabricated by electrophoresis, obtaining a ceramic material of density approaching 90 %.

The interest in beta-alumina revived in sixties when researches (specially those conducted by automotive concerns) were started to produce high-performance batteries for the drive system in motors for automotive vehicles. The batteries based on solid electrolyte of the sodium-sulphur type offered capacity many times higher than the batteries of acid type, e.g. the lead ones. The industry somehow ignored this project and only at the start of the 90-ties, wide-scale studies were initiated on this ceramic material. However, the studies were mainly focussed on designing of high-performance batteries. And it was then when they observed that at high temperatures of 800-900 °C during prolonged trials, the effect of ionic conductance is sometimes reduced, and when the trials take the time of several thousand hours, this effect is recurrent. The drop in ionic conductance is related with the formation of nanocracks, which form a path of high electric resistance. Prolonged roasting at very high temperatures results in closing of these nanocracks due to repeated roasting of the ceramic grains. So, a hypothesis has been developed which assumes that it is possible to recover the ionic conductance by roasting of material at a temperature of 1400 °C in vacuum during the time of 100 hours. After this process, the mechanical properties are improved [1, 3, 4, 5, 8].

Products made from "beta-alumina" are fast, polycrystalline ceramic materials which may hold the implanted mobile ions of Na, K, Ag, H, Pb, Sr, Ba, Li and oxygen. The ceramic materials conducting, among others, also sodium ions are available in the form of thin-wall tubes (of different dimensions), rods, disks and plates.

The main physical and electric properties of sodium ions-conductive "beta-alumina" are as follows:

- porosity: 1-2 %,
- average pore size: 1-5 µm,
- max. pore size: 8 µm,
- max. grain size: 20 µm,
- bending strength: 300 MPa,
- thermal expansion at :
- 0-500 °C => $7,2 \times 10^{-6}$,
- 500-1000 °C => $8,6 \times 10^{-6}$,
- ionic conductance at :
- 75 °C => $0,2 \text{ (ohm.m)}^{-1}$,
- 100 °C => $1,2 \text{ (ohm.m)}^{-1}$,
- 200 °C => $9,2 \text{ (ohm.m)}^{-1}$,
- 300 °C => 24 (ohm.m)^{-1} ,
- 400 °C => 38 (ohm.m)^{-1} ,
- 500 °C => 43 (ohm.m)^{-1} ,
- 600 °C => 49 (ohm.m)^{-1} .

For operation in liquid aluminium alloy most suitable seem to be the tubes (retorts) blind on one end and made from "beta-alumina" stabilised with zircon (containing about 6% ZrO₂), characterised by conduction of sodium ions. In this case, zircon raises the resistance of the ceramic material to thermal shocks which cannot be avoided under the conditions of the planned experiment. It should be observed that zircon reduces to a very small degree only the ionic conductance of this ceramic material.

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