

A new Electrochemical Sensor for the measurement of Sodium in Aluminium Alloys

Abstract

This paper presents a new electrochemical sensor for rapid real time measurement of sodium concentration in aluminium alloys.

The accuracy of this new Sodium sensor is compared to traditional methods of monitoring sodium such as spectrometer and thermal analysis.

Finally the potential of the new sensor to be incorporated into a device which can accurately control sodium level is described.

Introduction

Sodium has been used for many years to modify aluminium silicon alloys. However the modified structure presents the disadvantage of being unstable and tending to fade rapidly and therefore reverting to the unmodified condition.

It is therefore necessary to control the sodium level regularly to be sure that the castings properties remain constant.

Conventional techniques for the determination of sodium content are costly and intermittent, as there is usually some delay between sampling and the test result. Moreover the results are only valid for the time of the sampling.

To overcome this problem, a novel electrochemical sodium sensor has been developed, to give an immediate and real time sodium content in the melt.

Sodium levels can thus be controlled within much tighter specifications and the control of the metal properties of the finished casting can be more consistent.

The novel Sodium analyser : ALSPEK Na

Theory

The electrochemical sensor is based on a tube of a beta alumina solid electrolyte that contains a reference material. This acts as a Nernstian potentiometric cell in which the solid electrolyte separates the reference electrode (with a known activity of sodium) from the aluminium alloy with an unknown activity (concentration) of sodium.

The sodium sensor works on the Nernst principle :

$$E = - (RT/zF) * \ln (A_{working}/A_{reference})$$

Where :

E = Electrical potential

R = Molar Gas Constant (8.3144 Joule/mole Kelvin)

T = Absolute temperature (K)

z = number of electrons transferred in the system being measured

F = Faraday constant (96.485 coulombs/mole)

A_{working} = chemical activity of element in the melt

A_{reference} = chemical activity of reference electrode material (sodium)

This Nernst equation provides the theoretical relationship between the potential generated by the cell and the relative activities of the reference and working electrodes.

The plot of electrical potential (sensor voltage) versus the natural log of the ratio of elements activities of the working and reference electrodes yields a straight line relationship as shown in Figure 1.

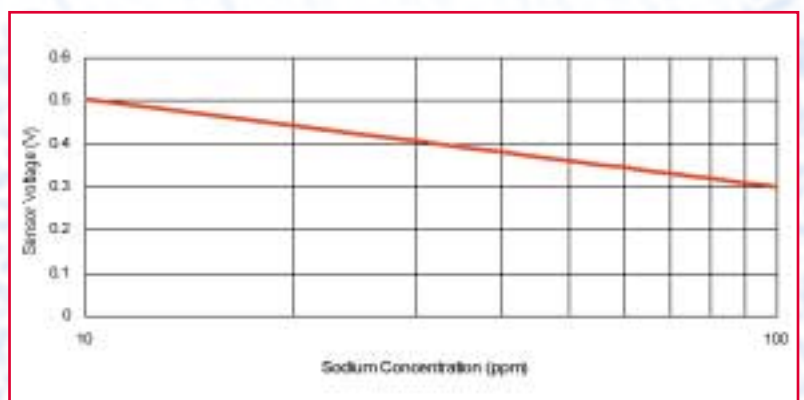


Figure 1: Sensor voltage v sodium concentration

Design of the sensor (figure 2)

Reference electrode

The material chosen as reference material is metallic sodium.

Metallic sodium has been selected because it responds to the criteria of giving rapid response and accurate measurement of sodium content.

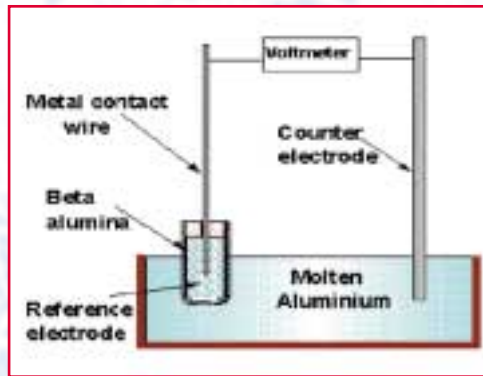


Figure 2: Schematic drawing of the sodium sensor

A hermetic refractory seal is used to protect the reference material inside the beta tube. It prevents air ingress into the compartment or sodium vapour leakage from it. This seal is corrosion resistant to high temperature sodium attack over extended immersion times.

Beta Alumina tube

The sensor head consists of a beta alumina tube which is an ionically conducting ceramic that separates the 2 electrodes.

In order to get a good thermal shock resistance, it has been designed in a small, thin walled tube and its inherent strength has been improved by the addition of a small quantity of zirconia.

Counter electrode

Silicon Carbide is the material chosen for the counter electrode contact because of its good electrical conductivity and corrosion resistance.

Design of the probe

In order to be used in foundries in molten aluminium and aluminium alloys, the sodium sensor requires a holder and a read out unit which displays the sodium concentration (figure 3).



Figure 3: Sodium sensor probe

The probe consists of several elements that are inner, washer, holder and the Read Out Unit.

The inner (Sensor core)

This inner has been designed to be easily removed when necessary (figure 4). It consists of the sensor itself with a lead wire attached to the reference electrode and internal thermocouple. The internal thermocouple allows automatic compensation with the Read Out Unit.

The inner is located inside the silicon carbide holder. It is connected to three screws in the sensor connection block (two connections are for the internal thermocouple and one is for the sensor). The connection for the counter electrode holder is already made internally.



Figure 4: Sodium sensor inner core

The washer

The sensor head requires a ceramic fibre washer attached to it to prevent aluminium from moving between it and the silicon carbide tube.

The holder

The holder is the silicon carbide/counter electrode tube.

The Read Out Unit (SSRU)

The Read Out Unit displays the sodium concentration in the aluminium bath in parts per million (ppm), depending on the voltage output from the sensor (figure 5). It is hand held and battery operated.

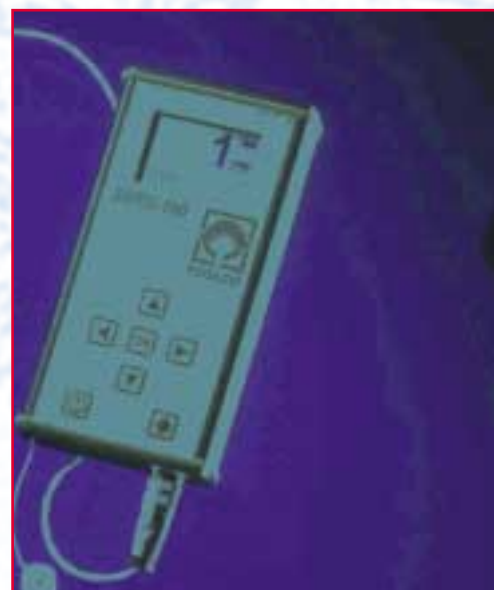


Figure 5: Sodium sensor read out unit

The Preheater

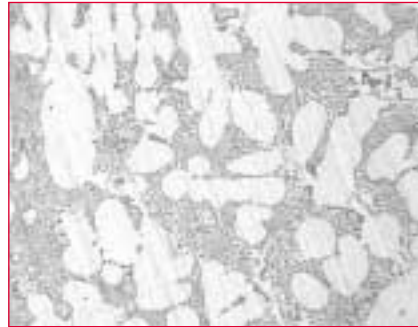
In order to avoid any thermal shock and failure, the sensor head will need to be preheated. The Read Out Unit has a temperature display which measures the sensor temperature directly and indicates when it is possible to immerse it into the aluminium bath (figure 6).



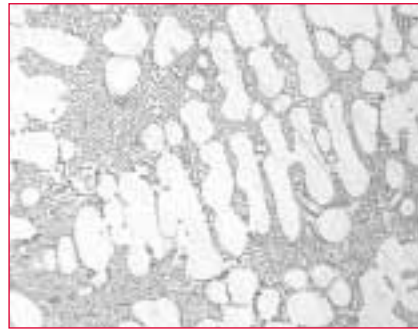
Figure 6: Preheat unit

Metallographic analysis

The results show the modification state in accordance with the sodium sensor result (figure 8).



Sample 1 : Al-Si 10 Mg
Na (sensor) = 51 ppm
Na (spectrometer) = 51 ppm
Eutectic structure



Sample 2 : Al-Si 10 Mg
Na (sensor) = 14 ppm
Na (spectrometer) = 13 ppm
Acicular structure

Figure 8: Comparison of measured Sodium level and metallographic analysis

Measurements and results

Response Time

The response time of the sodium sensor is approximately one minute after immersion into the aluminium bath.

Results

The results show the good accuracy between spectrometer and the sodium sensor, generally better than 10 ppm (figure 7).

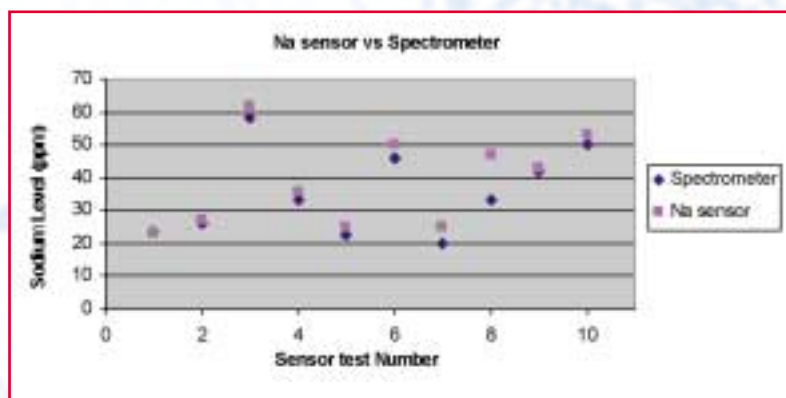


Figure 7: Comparison of Sodium sensor reading and Spectrometer

Thermal analysis

The results of thermal analysis are in accordance with the sodium sensor results (figures 9 and 10).

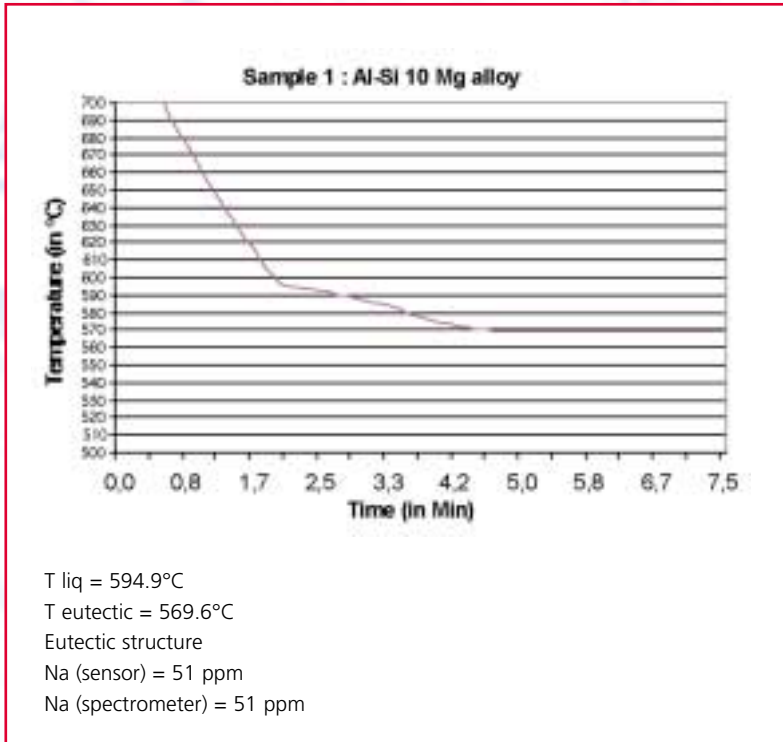


Figure 9: Comparison of measured Sodium level and thermal analysis

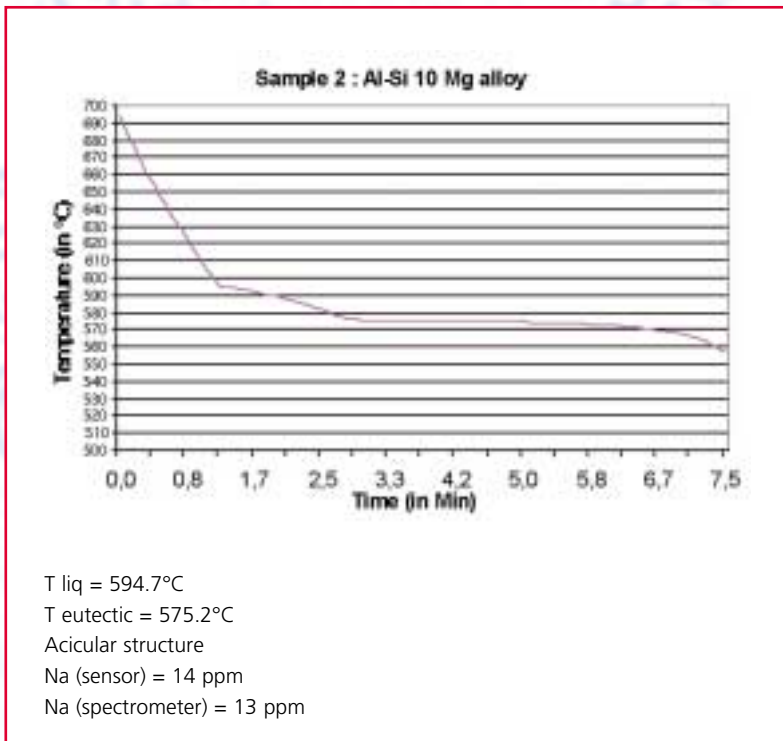


Figure 10: Comparison of measured Sodium levels with thermal analysis

Sodium sensor and COSMA

The new electrochemical sodium sensor can be incorporated into a device which can accurately control sodium level.

COSMA(COntrolled addition of Sodium Modifier to Aluminium) has been developed to control sodium modification and maintain a constant level of sodium by adding sodium at the rate required.

The combination of the sodium sensor with COSMA allows an automatic and continuous addition of a controlled amount of sodium to the aluminium bath.

Conclusion

This new electrochemical sodium sensor, ALSPEK Na, is easily usable in foundries for the control of sodium content in molten aluminium and aluminium alloys.

It can be used either for spot checks or continuously. It gives a rapid real time measurement of sodium concentration in aluminium baths and therefore saves time compared to traditional methods. It also gives a much tighter control of the modification process.

The sodium sensor can be connected to an additional unit (COSMA) to control the process of sodium modification in continuous use.

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