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Electrochemical sensor for measuring magnesium content in molten aluminium

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Design, construction, and tests of magnesium electrochemical sensors using molten salt electrolytes and pure magnesium metal reference are described. Alumina as well as magnesia membrane thimbles were synthesized to use as the supporting matrixes for the liquid electrolytes. Binary as well as ternary salt mixtures containing $MgCl_2$ were impregnated in thimbles of various pore sizes. The accuracy, response time, and service life of the sensors were evaluated. The magnesium contents from the electromotive force (e.m.f.) measurements were comparable with those from the atomic absorption analysis. All sensors responded instantly to the changes of magnesium concentration in aluminium melt. The service life was between 2 to 6 h and the minimum initial equilibration time was 2 min, depending mainly on the pore size of the magnesia thimble and the electrolyte salt mixture in use.

1. Introduction

In the aluminium industry, the control of the chemical composition of a metal with respect to alloy constituents as well as impurities is carried out while the aluminium is molten. The most commonly used technique for measuring the composition is spectrometric analysis on cast samples. Although it is rapid, this analysis is retrospective. Since the composition of the Al melt changes continuously, reliable online monitoring would be a significant step forward for rapid and accurate composition adjustment. Electrochemical sensors of galvanic cell construction, based on simple thermodynamic measurements, are one possible approach towards the online monitoring.

Encouraged by the success in measuring oxygen contained in steel bath, scientists world-wide are making electrochemical sensors for use in molten aluminium [1, 2] as well as in other molten metals [3, 4]. The development of sensors for measuring Mg in molten Al has been attempted, and the results are reported in this work.

2. Probe design

An electrochemical cell expressing the working principle of a sensor measuring element M in molten Al is

wire, M(ref)|M ion conductor|M (in Al), wire

At equilibrium, the Nernst equation applies for the galvanic cell:

$$-ZEF = RT \ln a_M / a_{M(\mathrm{ref})} \tag{1}$$

where Z is the units of charge carried, E is the potential (in V) between the two electrode leads measured with a high impedance voltmeter, F is the Faraday constant; R is the gas constant, T is the temperature (in K), a_M is the activity of M in the metallic solution, and $a_{M(\mathrm{ref})}$ is the activity of M in the reference.

The basic requirements [5] for such an electrochemical cell are: (1) that the electrolyte has sufficiently high ($> 10^{-3}\ \mathrm{S\,m^{-1}}$) ionic rather than electronic conductivity, and the latter, if any, should be less than 0.5% of the total conductivity; (2) that the activity of M in the reference material is reversible and only a function of temperature; and (3) that the cell can readily reach an equilibrium. Therefore, the electrolyte (M ion conductor) is the most important component of the sensor. The reference material and electrode leads need only to be considered when a suitable electrolyte is available.

The two known Mg^{2+} solid electrolytes, Mg-β'' alumina [6] and $MgZr_4(PO_4)_6$ [7], were prepared in the laboratory, and their compatibility with pure Al and Al–Si alloy was investigated. Both materials were found to deteriorate through chemical reactions shortly (< 0.5 h) after dipping in the Al–Si alloy, though their chemical stability in pure molten Al was slightly higher. Both electrolytes were thus considered unsuitable for use in molten Al. Instead, fused salts containing Mg^{2+} were employed. Consequently, pure Mg metal was chosen as the reference, and Mo wire as the lead for the reference electrode since Mo is chemically stable in the salts as well as in the metal reference.

Mixtures of $CaCl_2 + MgCl_2$ have been used in the work of Tiwari and Howie [8]. The salt mixture was placed on an alumina frit, and pure Mg metal reference was held using a Mo capsule immersed in the fused salt to prevent Mg from oxidation. In this work, instead of using alumina frit plates, alumina as well as magnesia membrane thimbles were synthesized to use as the supporting matrix for the liquid electrolyte. The salt mixture was infused into the thimbles of different pore sizes prior to use.

When Mg metal was used as the reference, its solubility in the salt mixture was a concern. Comprehensive information on the solubility of metal in its halides is not readily available. However, it is known [9] that the solubility of Mg in $MgCl_2$ is less than 0.5 mol % at 800 °C, and that in other salts can only result from its displacement reaction with the cations of the salts. Thermodynamic calculations indicate that Mg can replace neither Li in LiCl nor K in KCl. Therefore, it is believed that the miscibility of Mg with the mixture of $MgCl_2 + LiCl(+KCl)$ is negligibly small and the overall electronic conductivity by Mg in the salt mixture is sufficiently low to meet the requirement of a galvanic cell.

2.1. *Initial tests with alumina thimbles*

Three types of porous alumina thimbles (pore size: 1, 2.5, and 6 μm) were prepared from two sized alumina powders. These thimbles were immersed in salt mixtures in order to assess the result of salt impregnation. There was no problem for salt mixtures of various compositions to enter the pores of these thimbles. Since alumina thimbles were found to react with the Mg metal reference, they were abandoned in favour of magnesia thimbles. Alumina cement was also avoided for the same reason.

2.2. *Preparation of MgO membrane thimbles for salt impregnation*

Through a simple pressing-and-sintering route, MgO thimbles (type A) of large pore size ($>5\,\mu$m) were obtained from a fused MgO powder of $-50\,\mu$m particle size (Aldrich Chemicals); and thimbles (type B) of small pore size ($<0.2\,\mu$m) from a 'heavy' MgO (BDH Ltd). Types A and B thimbles have similar overall dimensions. The external diameter is 8 mm, the wall thickness is 1.5 mm, and the length is 35 mm. After repeated firing-and-grinding, MgO powder was also hot-pressed and sintered to thimbles (type C) of $1 \sim 2\,\mu$m pore size. Type C thimbles are slightly tapered, and the external diameter is 10 mm at the open end and 8 mm at the close end. The length is 60 mm, and the wall thickness is 2 mm.

Even with a pore size greater than 5 μm, type A thimbles were found to have sufficient mechanical strength in Al–Mg melts prior to salt impregnation.

2.3. *Salt mixture*

$MgCl_2$ was used as the necessary Mg^{2+} conducting component of the liquid electrolyte. Other reasons for using this salt are the low cost, low vapour pressure, and low toxicity compared with other magnesium halides. To ensure a liquid electrolyte at a temperature as low as 650 °C at which some Al alloys start to melt, one or more salts are required to mix with $MgCl_2$ (m.p. 714 °C) to form a eutectic mixture. The candidate salts to mix with $MgCl_2$ are $CaCl_2$, LiCl, and KCl. First of all, $CaCl_2$ has many similar properties to $MgCl_2$, and has been used in developing Mg sensors [8]. Molten LiCl has a low specific gravity, and is useful to form a salt mixture lighter than the Mg metal reference. This mixture is thus able to float on the reference as a protective layer in addition to function as an electrolyte. KCl is the least hygroscopic, and is favoured for Mg probes applicable particularly in air atmosphere. The composition of the salt mixtures can be read, for a desired melting point, from the binary phase diagrams [10]. For a melting point of $650 \sim 670$ °C, a $MgCl_2$ mass content of $18 \sim 24\%$ is required for the $KCl + MgCl_2$ mixture. It should be mentioned that the mixture with a $MgCl_2$ mass content of $78 \sim 82\%$ also has a similar melting point. However, the mixture with a lower $MgCl_2$ content was used to alleviate the hygroscopic problem of the salt mixture since KCl is much less hygroscopic than $MgCl_2$.

$LaCl_3$ was also added to $MgCl_2$ and the above binary salt systems in order to investigate its effect on the response time (particularly the equilibration time upon first dipping) and the service life of the sensors.

When $LaCl_3$ was involved, the mass ratio of the binary mixture was determined from the $LaCl_3$–$MgCl_2$ phase diagram [11]. However, for ternary salt systems, there is no well-defined phase diagram for choosing the mass ratio of, for example, $KCl{:}MgCl_2{:}LaCl_3$. The closest information available is possibly that of the KCl–$MgCl_2$–$CeCl_3$ system [10]. In our case, the mass ratio of $KCl{:}MgCl_2{:}LaCl_3$ was chosen approximately referring to this phase diagram.

When the ratio was chosen, salts were weighed and mixed in a glove box, ready for impregnation.

2.4. *General assembling procedure of Mg probes*

The general construction of the sensors is illustrated in Fig. 1. Porous MgO thimbles were filled with pure Mg metal chips, and Mo wires were inserted down to the inside bottom. In most cases, the thimbles were also sealed with cement (940 zirconia based, Cotronics Co.). The probes (except probe 2) were then extended with short alumina tubes that are subsequently filled with the electrolyte salt mixture. Under purified argon gas, these probes were immersed into a molten salt mixture for impregnation at 725 °C for $0.5 \sim 3$ h. The actual time of impregnation was determined by the porosity of the MgO thimbles and the salt mixture in use. For instance, 0.5 h was used to infuse $LiCl + MgCl_2$ into thimbles of $>5\,\mu$m pore size (type A); whereas $2 \sim 3$ h were used to infuse $LaCl_3 + KCl + MgCl_2$ into thimbles of 0.2 μm pore size (type B). The probes were lifted out of the salt

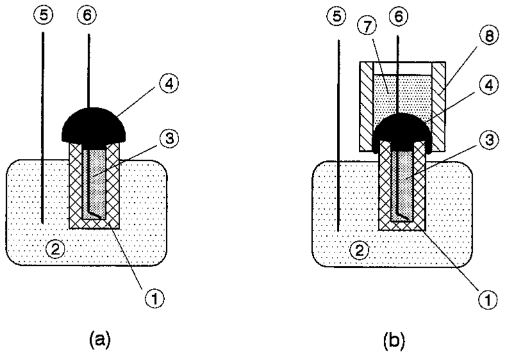

Fig. 1. Schematic construction of the Mg sensors, (a) without alumina extension tube; (b) with alumina extension tube and salt seal. (1) Porous MgO thimble impregnated with molten salt electrolyte, (2) Al–Mg melt, (3) Mg metal, (4) cement, (5) steel or graphite bar, (6) Mo wire, (7) salt layer, and (8) alumina extension tube.

bath before the temperature was brought down. After cooling to room temperature, these probes were stored in containers filled with argon gas. During handling, efforts were taken so that the probes would be exposed to air for as short as possible periods of time. A stainless steel or graphite bar protected with an alumina tube was used as the lead in molten Al. Such a lead is inexpensive, and is chemically stable in this specific situation.

2.5. *Preparation of Al-Mg alloys and change of Mg content*

Al–Mg alloys of about 250 g were, in most cases, premade by melting pure Mg (99.99%) and Al (99.85%) metals together in a graphite-coated porcelain crucible under argon atmosphere. A temperature higher than the melting points of the metals was maintained for at least two hours to obtain alloys of uniform composition.

The change of Mg content in the Al–Mg alloy during the tests was made *in situ* by adding Mg-rich Mg–Al alloy pieces or pure Al metal chips.

3. Tests and evaluation of Mg sensor performance

During the tests under argon at a constant temperature, no attempt was made to change the Mg content, whereas during the tests in air, the Mg content was varied while the temperature was kept constant.

The Mg content indicated by the e.m.f. (E) of the sensor at a temperature T was calculated from the following equation given by Tiwari and Howie [8]:

$$\left[\frac{E}{T}\right] = 0.2029 - 0.0996\log(\text{wt\% Mg}) \pm 0.0043 \quad (2)$$

where $[E/T]$ is in mV K^{-1}.

The atomic absorption (AA) was used to analyse the Mg content in Al on the samples taken during the tests. Samples of 0.125 to 0.5 g each were dissolved in acid of 25 cm^3 and subsequently diluted up to 10 times for the analysis. It should be noted that the accuracy of the chemical analysis in this case was quite low (about ±0.01 wt% Mg in Al). Therefore, the results of chemical analysis served only as a rough indication rather than accurate reference for the performance of the sensors.

4. Test results and discussions

Batches of probes have been made and tested. The following are the typical performance in relation to construction and test conditions.

4.1. *Tests under argon*

Instead of sealing the Mg metal reference with cement, a salt mixture lighter than Mg metal was used as a protective layer covering the reference. With a mass ratio of LiCl:$MgCl_2$ of 4:1, the mixture has a eutectic point of 590 °C according to the phase diagram [10].

Thimbles of type A ($>5\,\mu m$ pore size) were filled with Mg metal chips and then cemented to short alumina extension tubes. Prior to impregnation, the extension tube was also packed with salt mixture of same composition to the electrolyte.

It was found by sectioning the probe end after salt impregnation that the Mg metal was well protected from oxidation underneath a salt layer of about 20 mm in the alumina extension tube.

To conduct the tests, the probe was mounted over the pre-formed Al–Mg alloy in a sealed Inconel vessel before the vessel was heated up. While the molten alloy was kept to a set temperature, the probe was lowered to the Al–Mg alloy and the e.m.f. of the sensor was recorded immediately.

Figures 2 and 3 show the e.m.f.s of the following electrochemical cell with probes 1a and 1b:

$$(+)\ \text{Steel or C, Al–Mg}|\text{LiCl} + \text{MgCl}_2$$
$$\text{in porous MgO thimble}|\text{Mg, Mo}\ (-)$$

Probe 1a. At a temperature of 687 °C, probe 1a (Fig. 2) reached a stable e.m.f. of 115.2 mV in about 20 min, and this e.m.f. reading remained for about 60 min. Although the temperature and Mg content were kept constant, the e.m.f. started to decrease, which is a sign of probe failure.

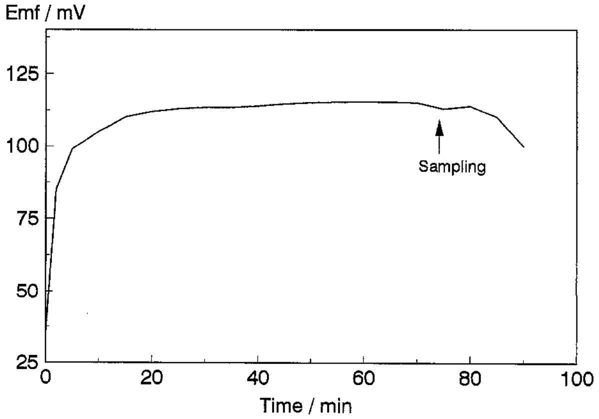

Fig. 2. E.m.f. of probe 1a. Salt mixture ($MgCl_2$ + LiCl) and mass ratio 1:4; thimble type: A; counter electrode: graphite; working temperature: 687 °C; under argon.

The Mg content at the equilibrium e.m.f. of 115.2 mV corresponds to a Mg content of 6.699 wt % according to Equation 2. The Mg content of 6.711 wt % of this alloy was obtained from the chemical analysis, which is fairly close to the Mg content from the e.m.f. measurement.

Probe 1b. Probe 1b took slightly longer to reach a stable e.m.f. at 687 °C (Fig. 3), but remained fairly stable once it did, apart from a fluctuation of about 10 mV at about 80th minute. A failure pattern similar to that of probe 1a was found. The chemical analysis on a sample taken at the end of test revealed a Mg content of 0.303 wt %, which is close to 0.298 wt % calculated from the e.m.f. measurement.

Generally speaking, the sensors of such configuration responded to the Mg content on the first dipping rapidly. The equilibrium e.m.f.s indicated accurately the Mg content in the Al melt. However, the service life of such sensors was less than 2 hours as a result of the salt loss. This is due to: (i) the large pore size of the thimbles, and (ii) the low viscosity of LiCl. Therefore, for sensors to use in air atmosphere, thimbles of smaller pore sizes and less hygroscopic KCl were used.

4.2. *Tests in air atmosphere*

The Mg reference inside the porous MgO thimble was covered with cement and then the salt electrolyte was filled in the short alumina extension tube as an extra seal to the reference. The salt electrolyte was then infused into the MgO thimble. The Mo wire was protected from oxidation by sealing it in a thin silica tube, and the whole assembly was stored in a container filled with argon gas.

When the alloy became molten and the temperature reached a preset value, a probe was taken out of the storage container, hung over the melt for about 5 min and then dipped into the melt for e.m.f. measurements. Figs 4–8 show the e.m.f. measurements on the following electrochemical cell with Probes 2, 3, 4, 5, and 6:

$$(+)\ \text{Steel or C, Al–Mg}|(LaCl_3 + KCl) + MgCl_2$$
$$\text{in porous MgO thimble}|\text{Mg, Mo}(-)$$

The temperature was kept constant throughout, and samples were taken for chemical analysis before the Mg concentration was altered. There was always a minor temperature fluctuation upon taking a sample or changing the Mg content. But the e.m.f. change as a result of Mg concentration variation was much more pertinent.

The main problems for sensors in air were the protection of Mg metal and Mo wire from oxidation and the retention of salt electrolyte in the pores of the thimbles. In order to find out the service life, all probes were tested until failure.

Probe 2. The thimbles (type C) filled with Mg metal reference and sealed with Cotronix 940 were impregnated with a salt mixture of $KCl + MgCl_2$ (mass ratio 2.4:1). Alumina short extension tubes were not used in this batch of probes. During the test, the probe was positioned so that the MgO thimble was partially immersed in the Al melt. At 710 °C, probe 2 responded to the low Mg content of the alloy on its first dipping with a high value of e.m.f. (Fig. 4). Upon addition of Mg, the e.m.f. decreased instantly, and then increased slowly with time possibly due to the Mg loss in the melt. When a piece of pure Al was added, the e.m.f. increased sharply and then resumed the slow increase with time. The e.m.f. signal became fluctuated when the melt was stirred, and the thimble was found to be broken.

The initial low Mg content of Al melt was far outside of the accuracy of chemical analysis. For the subsequent samples, the Mg contents indicated by the e.m.f.'s were 0.412, 0.129, and 0.087 wt %, and by the chemical analysis were 0.264, 0.155, and 0.092 wt %, respectively. Although there is a significant difference between the chemical analysis and e.m.f. measurement for the first sample, it is encouraging to see that the sensor responded rapidly to the

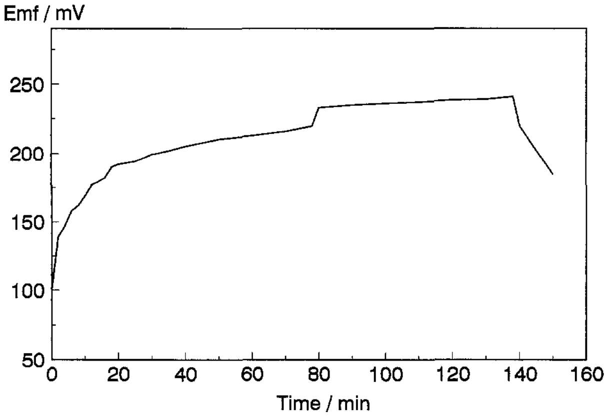

Fig. 3. E.m.f. of probe 1b. Salt mixture, mass ratio and conditions as for Fig. 2.

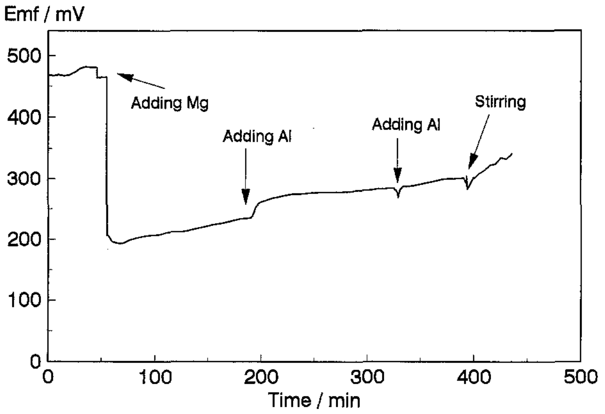

Fig. 4. E.m.f. of probe 2. Salt mixture ($MgCl_2 + KCl$) and mass ratio 1:2.4; thimble type: C; counter electrode: steel; working temperature: 701 °C; no extension tube, partial immersion.

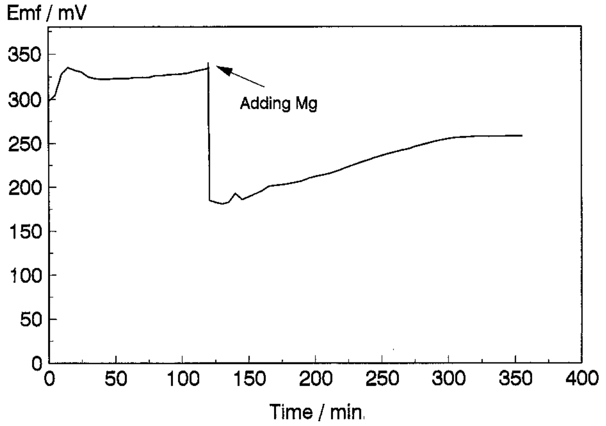

Fig. 5. E.m.f. of probe 3. Salt mixture ($MgCl_2 + KCl + LaCl_3$) and mass ratio 1:2:0.3; thimble type: B; counter electrode: graphite; working temperature: 705 °C; with alumina extension tube.

change of Mg content and was fairly accurate at later stage of the measurement. The total working time of this probe was about 6 hours.

Probe 3. The MgO thimbles used were those of type B ($< 0.2\,\mu m$). Short alumina extension tubes were used. The salt mixture was $LaCl_3 + KCl + MgCl_2$ (mass ratio 0.1:2.5:1) of very small amount of $LaCl_3$. At 705 °C, the e.m.f. of probe 3 (Fig. 5) instantly reached 300 mV, and then increased slowly again with time. A sample was taken at 334 mV, followed by Mg addition. The e.m.f. came down sharply to 185 mV, and became stable at around 184 mV before increasing slowly again with time. The probe head came off at about the 6th hour, also as a result of Mo wire oxidation and subsequent wire breakage. A final sample was taken corresponding to an e.m.f. of 258 mV. For these two samples taken, the Mg contents by e.m.f. measurement were 0.041 and 0.191 wt %, and those by chemical analysis were 0.023 and 0.193 wt %, respectively. Again, the discrepancy between the chemical analysis and sensor reading became less significant at later stage of the test. It showed that the involvement of small amount of $LaCl_3$ in the salt mixture did not have significant effect on the performance, particularly on the initial equilibration time of the sensor.

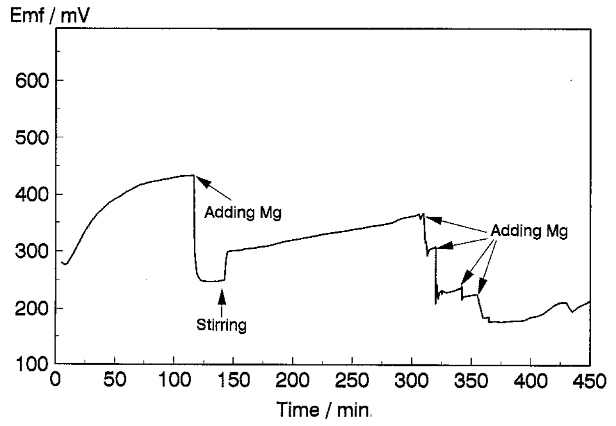

Fig. 6. E.m.f. of probe 4. Salt mixture ($MgCl_2 + KCl + LaCl_3$) and mass ratio 1:5.5:0.6; thimble type: B; counter electrode: steel; working temperature: 688 °C; with alumina extension tube, probe left for overnight.

Probe 4. MgO thimbles of type B (pore size $< 0.2\,\mu m$) were used. The salt mixture used for the impregnation was $LaCl_3$:KCl:$MgCl_2$ = 0.6:5.5:1 (mass ratio). The content of $LaCl_3$ was increased and that of $MgCl_2$ decreased compared with the previous test batch. At 688 °C, the initial response of the sensor to the low Mg content was slow (Fig. 6), but later it did respond instantly to the addition of Mg. While the melt was left undisturbed for 20 min, the e.m.f. was steady at 250 mV. After the melt was stirred, the e.m.f. increased rapidly to 300 mV and then kept increasing slowly with time. The e.m.f. was also instantly brought down by the addition of Mg. This procedure of taking sample and adding Mg was repeated. The e.m.f. became fluctuated at the 5.5th hour, indicating the probe failure. When lifted out after 13 hours of e.m.f. reading, the outside of MgO thimble was found covered by a layer of black material. This might be the reason of fluctuated e.m.f.. Some values of Mg content from the e.m.f. measurements were 0.067, 0.373, 0.474, 1.519 wt %, and those by the chemical analysis were 0.056, 0.160, 0.484, 1.382 wt %, respectively. Generally speaking, similar performance was found to the previous sensors, although the $LaCl_3$ content used in the salt mixture was higher.

Probe 5. MgO thimbles were of type B (pore size $< 0.2\,\mu m$). The salt mixture was $LaCl_3$:KCl:$MgCl_2$ = 5:6:4 (mass ratio). After 3 h of salt impregnation, the thimbles were found severely corroded. Probe 5 (Fig. 7) appeared to be fairly fragile but managed to remain intact for the test. In an aluminium melt at 690 °C, the e.m.f. steadily climbed up to 400 mV in 40 min. At an e.m.f. of 424 mV, the probe was lifted out. A second immersion resulted in a rapid equilibrium in about 15 min and the same e.m.f. value was obtained. There were minor fluctuations throughout. The Mg content was 0.004 wt % from both the e.m.f. measurement and the chemical analysis.

Probe 6. When $LaCl_3$ only was used to mix with $MgCl_2$ as the electrolyte of Mg sensors, the mass

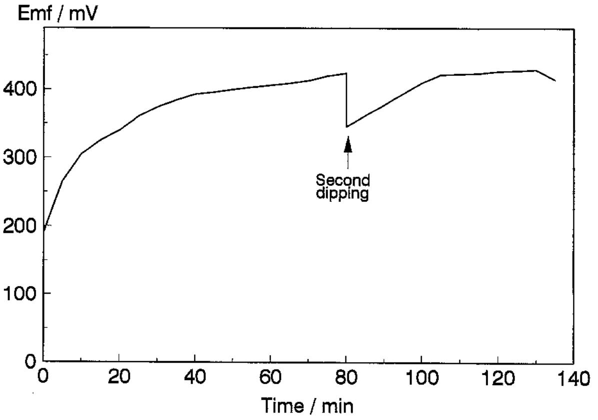

Fig. 7. E.m.f. of probe 5. Salt mixture ($MgCl_2 + KCl + LaCl_3$) and mass ratio 4:6:5; thimble type: B; counter electrode: steel; working temperature: 690 °C; Mo wire broken due to oxidation.

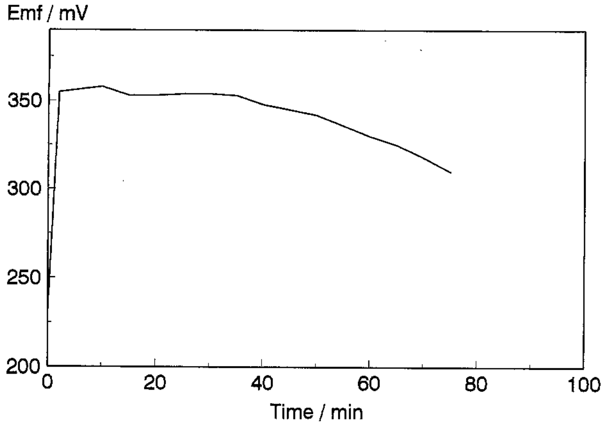

Fig. 8. E.m.f. of probe 6. Salt mixture ($MgCl_2 + LaCl_3$) and mass ratio 1:1.1; thimble type: C; counter electrode: graphite; working temperature: 725 °C; no extension tube, Mg ref. oxidation.

ratio of $LaCl_3$:$MgCl_2$ was 1.1:1. MgO thimbles of type C (pore size is 1 ~ 2 μm) were used. Before the test, severe oxidation of the salts occurred as a result of hygroscopic reaction during handling. A thick oxide layer was seen at the probe tip around the MgO thimble. Probe 6 had an e.m.f. of 355 mV in less than 2 minutes after dipping into the melt at 725 °C, but started to decrease immediately (Fig. 8). After 40 min, the e.m.f. decreased dramatically, indicating the probe failure. No sample was taken for chemical analysis. It can be seen from this test that the initial response of the probe was very rapid, but the life of the probe was short.

In the case of the salt seal held in a short alumina extension tube, the Mg metal reference was always found intact from oxidation. This ensures the primary success in making Mg probes to use in air atmosphere. The failure of these sensors was mainly due to the loss of salt from the pores of MgO thimbles, and, occasionally, Mo wire oxidation. Solving these problems may be regarded as a part of the future work on this project.

4.3. *Summary*

Comparing the e.m.f.–time charts of probes tested under argon (Figs 2 and 3) and air atmosphere (Figs 4–8), the e.m.f. of sensors under argon remained easonably stable once an equilibrium was achieved; whereas those in air generally shifted up slightly with time. This indicates the greater Mg loss in the Al melt when exposed in air, most likely due to oxidation rather than evaporation. Since there should be very little Mg oxidation under purified argon, the very little evaporation was confirmed from the very stable e.m.f.'s. The construction, test condition, and performance of the above sensors are summarized in Table 1.

5. Conclusions

Mg sensors using molten salt electrolytes impregnated in ceramic membrane thimbles were studied. After initial equilibration, the sensors responded instantly to changes in Mg content. For a wide range of Mg content (0.004 ~ 6.7 wt %), good performance of the sensors on Mg measurement was confirmed with the chemical analysis. Mg metal reference of the sensors was well protected from oxidation with a layer of cement holder and an upper layer of salt seal.

The pore size of the thimbles plays a more important role in the initial equilibration of the sensors than the salt composition. The sensors from thimbles of small pore size have a long initial equilibration time; those from thimbles of large pore size have a short initial equilibration time. Among the three types of the thimbles tested, the pore size of 1 ~ 2 μm (thimble type C) is the most suitable in terms of salt impregnation and retention. The pore size of > 5 μm (thimble type A) is too large, whereas that of < 0.2 μm (thimble type B) is too small.

LiCl can be used to form a $LiCl + MgCl_2$ mixture lighter than Mg metal. This mixture is thus able to

Table 1. Summary on sensor construction, test condition, and performance

Probe	*Thimble type*	*Salt mixture*	*T* /K	*E.m.f.* /mV	*Mg from e.m.f.* /w/o	*Mg from AA* /w/o	*E.m.f. from AA* /mV	*Notes*
1a	A	$LiCl + MgCl_2$	960	115.2	6.699	6.711	115.1	service life 80 min, accurate
1b	A	$LiCl + MgCl_2$	960	245.0	0.298	0.303	244.4	service life 140 min, accurate
2	C	$KCl + MgCl_2$	974	235.0	0.412	0.264	253.7	no extension tube, not equilibrated
				283.9	0.129	0.155	276.2	towards equilibration
				300.5	0.087	0.093	297.9	reading close, service life 400 min
3	B	$LaCl_3 + KCl + MgCl_2$	978	334.0	0.041	0.023	358.0	not equilibrated
				258.0	0.191	0.193	268.0	reading close, service life 350 min
4	B	$LaCl_3 + KCl + MgCl_2$	961	307.6	0.067	0.056	315.0	third sample, reading close
				236.0	0.373	0.160	271.2	short time after Mg addition
				226.0	0.474	0.484	225.2	reading close
				177.6	1.519	1.382	181.5	reading close, service life: 330 min
5	B	$LaCl_3 + KCl + MgCl_2$	963	430.0	0.004	0.004	427.5	response slow
6	C	$LaCl_3 + MgCl_2$	998	–	–	–	–	Instant equilibration, probe life 30 min

float on the Mg reference and protect it from oxidation. Such sensors are able to measure the Mg content accurately and rapidly. However, they are not suitable for use in air due to the highly hygroscopic nature of the salts.

$LaCl_3$ has been proved unsuitable to use as an electrolyte component in such sensors due to the high viscosity, hygroscopicity, and the high reactivity with MgO. The effect of $LaCl_3$ in speeding up the initial equilibration is not as significant as that of appropriate pore size of the thimbles.

KCl is the most suitable salt component being the least hygroscopic and of appropriate viscosity. It thus plays an important role in extending the service life of sensors, particularly of those to use in air.

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References

[1] P. C. Yao and D. J. Fray, *Metall. Trans.* **16B** (1985) 41.

[2] S. Larose, A. Dubreuil and A. D. Pelton, *Solid State Ionics* **47** (1991) 287.

[3] D. J. Fray, *in* 'Extraction Metallurgy '81', IMM, London (1981) p. 321.

[4] D. J. Fray, *Benelux Metallurgie* **30** (1990) 63.

[5] R. V. Kumar and D. J. Fray, *in* 'Extractive Metallurgy '89', IMM, London (1989) p. 315.

[6] J. Kirchnerova, C. W. Bale, A. D. Pelton and A. Petric, *Mat. Res. Bull.* **26** (1991) 527.

[7] A. Kazakos-Kijowski, S. Komarneni, D. Agrawal and R. Roy, *ibid.* **23** (1988) 1177.

[8] B. L. Tiwari and B. J. Howie in 'Light Metals' Proc. Tech. Sessions TMS Light Metals Committee, 118 TMS Annual meeting, Las Vegas, NV, Met. Soc. AIME, Warrendale, PA, (1989) pp. 895–902.

[9] M. Blander (Ed.), 'Molten Salt Chemistry', Interscience Publishers, New York (1964).

[10] E. M. Levin, C. R. Robbins and H. F. McMurdie in 'Phase Diagrams for Ceramists' edited by M. K. Reser, Vol. 1 (1964) and Vol. 2 (1969) (American Ceramic Society).

[11] Von G. Vogel and A. Schneider, *Inorg. Nucl. Chem. Lett.* **8** (1972) 513.