

Effects of Sr-modification and melt cleanliness on melt hydrogen absorption of 319 aluminium alloy

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The effect of Sr-modification on hydrogen content of commercial 319 aluminium alloy melts has been quantified, by using HYSCAN instrument at 685°C and 735°C. In addition, the effect of melt cleanliness on the hydrogen content of the melt has been studied. It has been found that the melt cleanliness has a significant effect on the reduction of hydrogen content of the melt. The hydrogen contents of Sr-modified cleaned melts were significantly lower (30–45%) than uncleaned melts (melts containing surface oxide layers) at both temperatures. Sr-modification had no marked effect on the hydrogen content of the melt at both temperatures, when measurements were carried out in a cleaned melt. Hydrogen content of strontium modified, uncleaned melts has been increased, particularly at 685°C. In order to study the melt hydrogen absorption susceptibility in Sr-modified alloys, the formation of different hydrogen containing compounds such as hydrides and hydroxide of modifiers and other alloying elements in Al-Si melts has been evaluated thermodynamically. It has been found that there is no hydrogen containing compound, which can form in aluminium melts, and if these compounds are introduced into the melt they will dissociated to release hydrogen. © 2003 Kluwer Academic Publishers

1. Introduction

The modification treatment of Al-Si alloys is associated with an increase tendency to porosity formation [1–7]. It has been suggested that strontium and sodium increase the porosity by increasing the susceptibility of Al-Si melts to hydrogen absorption [8–12]. Denton and Spittle [8] and Honer and Youling [9] have claimed that Sr-modified melts are more susceptible to gassing than Na-modified ones. They have suggested that oxidation of strontium during melting causes the structure of the surface oxide layer to change and become more susceptible to hydrogen absorption. Bian *et al.* [10] by using HYSCANII instrument have shown that Sr-addition markedly increases the melt hydrogen content and accelerates the gassing rate of the Al-Si melts. Contrary, Gruzleski *et al.* [1, 13–16] and Kotte [17] have shown that Sr-modification has no considerable effect on the melt hydrogen content of A356 alloy. Gruzleski *et al.* have also indicated that Sr-modification does not affect the rate of regassing and degassing of A356 melt. In addition, some researchers have shown that a reduction in the melt hydrogen content takes place after modification treatment [18–20]. Recently, Guthy *et al.* [18] have indicated that a significant change in the hydrogen content of the melts with the level of strontium and sodium can occur. They have claimed that contrary to current views, accurate and repeated measurements using ALSCAN indicate a reduction in hydrogen levels

with modification. The observed reduction in hydrogen levels has been explained in terms of measurable changes in the melt's surface energy due to modifier additions.

Some authors have suggested that the modification by Sr and Na increases the susceptibility of melt to adsorb hydrogen by the formation of hydrogen containing compounds, not necessarily taken into account by recirculating hydrogen measurement techniques [21–23]. Garet *et al.* [21] have suggested that the hydrides, such as SrH₂ and NaH are present in the Na- or Sr-containing alloys and decompose during solidification to release hydrogen. Garet *et al.* have also indicated that the inclusions present in the Na- or Sr-modified melts can retain the hydrogen adsorbed on their surface and can increase the tendency to microporosity formation. Iwahori *et al.* [22] have studied the rate of vacuum degassing of Na- and Sr-modified melts. They have found that the hydrogen content of an unmodified or Na-modified melt is readily decreased by degassing, whilst that in a Sr-modified melt decreases only slightly. This was considered to be because the hydrogen adsorb into the oxide in the melt is more strongly fixed in the oxides by addition of strontium to the melt. Contrary, Gruzleski *et al.* [13] have shown that the Sr-modification does not increase the susceptibility of melt to adsorb hydrogen by formation of hydrogen containing compounds. They added pure strontium, covered

with 7.8%wt Sr(OH)₂ and 90%Sr-10%Al covered with 2.3%wt Sr(OH)₂ on their surface into the A356 melt. According to their Telegas measurements, they reported that there was no marked increase in hydrogen content. They have presumed that the Sr(OH)₂ “burns” at the melt surface so that hydrogen is not actually introduced into the liquid through the hydroxide. In addition, they reported that there is no evidence to support the hypothesis of formation of hydrides compounds in Sr-modified melts.

The aim of present study is to evaluate the hydrogen absorption behaviour of Sr-modified 319 Al-alloy. In addition, the effect of Sr-modification on the melt susceptibility to hydrogen absorption has been studied by using HYSCAN instrument and thermodynamic studies. The formation of different hydrogen containing compounds such as hydrides and hydroxide of modifiers and other alloying elements in Al-Si melts has also been evaluated by thermodynamic studies.

2. EXPERIMENTAL METHOD

2.1. Materials and melting

Five kilograms of 319 Al-alloy ingots were melted in a gas fire furnace with a silicon carbide crucible. The chemical composition of the alloy is given in Table I. Modification treatment and melt sampling for hydrogen content measurement were carried out at temperatures of 685°C and 735°C without degassing treatment. At first, several hydrogen measurements were carried out over a period of 65 min in unmodified melts. Then melts were modified with 0.03 wt% Sr using Al-10%Sr master alloy. Strontium addition was carried out by placing Al-10%Sr master alloy particle on the melt surface. (About 90% of floated strontium master alloy was submerged). Twenty minutes was considered for dissolution of strontium. The melt was stirred slowly after dissolution of strontium. Hydrogen content of the modified melt was measured continuously during a period of 60 min. Melt sampling for hydrogen measurements were carried out by use of a stainless steel cup after removal of surface oxide layer to take clean melt with minimum content of oxides. The stainless steel cup was preheated at 700–730°C prior to the sampling. In some cases in order to evaluate the effect of surface oxide layer on hydrogen absorption, the melt samplings were carried out by taking uncleaned melt from melt surface.

2.2. Hydrogen content measurement

Hydrogen content measurements were carried out in situ by using a HYSCAN instrument. The HYSCAN method is based on a quantitative reduced pressure technique to determine the hydrogen content. A sample of the molten alloy (100 g) is poured into a small

stainless steel chamber and the pressure reduced within several seconds to 0.1 mbar by a vacuum pump. The chamber and associated vacuum system is then isolated automatically from the pump and the sample allowed to solidify under reduced pressure condition. The operating pressure is 2 to 3 orders of magnitude lower than the traditional, qualitative reduced pressure tests, and this encourages that during controlled solidification of the sample, most of the hydrogen is released. The measurement can be carried out within 5 min.

3. Results and discussion

Fig. 1 shows the hydrogen content of the melt versus holding time for an unmodified and Sr-modified melt at 685°C. The same diagram at 735°C is shown in Fig. 2. It is seen that the hydrogen content of the melt was in the range of 0.20–0.24 ml/100 g Al at 685°C and 0.26–0.29 ml/100 g Al at 735°C for both modified and unmodified alloys. There was no marked increase in hydrogen content after Sr-modification treatment. As many authors have indicated [13, 21–23], it is important to consider that strontium has a high propensity to form hydrogen containing compounds such as SrH₂ and Sr(OH)₂. The Gibbs free energies of formation of different type of hydrides and the stability temperatures of different type of hydroxides probable in aluminium melt is presented in Tables II and III [24, 25]. The quantity of $K_{298^{\circ}\text{K}}$ in Table II is the

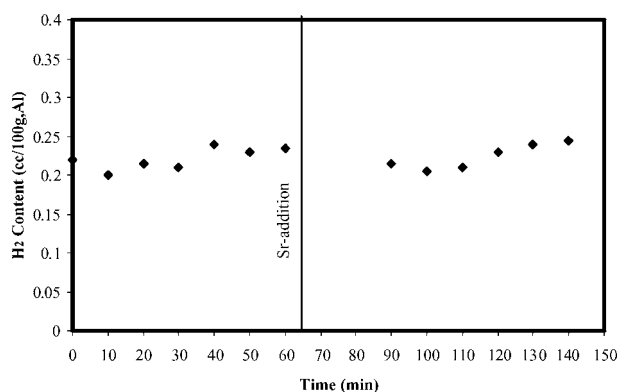


Figure 1 Variation of hydrogen contents vs. holding time before and after Sr-addition at 685°C.

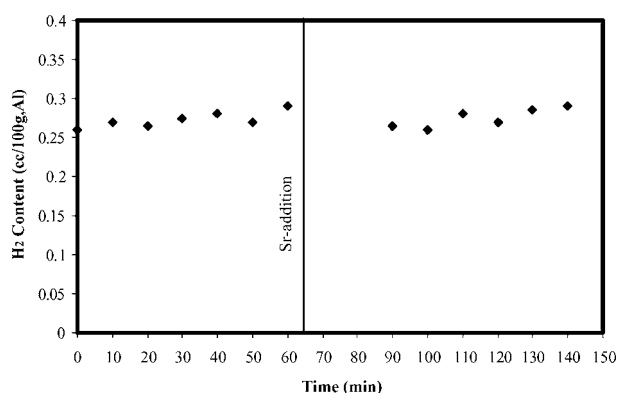


Figure 2 Variation of hydrogen contents vs. holding time before and after Sr-addition at 735°C.

TABLE I Composition of 319 Al-alloy used in the present study

Si	Fe	Cu	Mg	Zn	Mn	Ti	Al
5.82	0.31	3.45	0.38	0.11	0.23	0.12	Bal

TABLE II Thermochemical properties of different hydrides [24, 25]

Element	Hydride	Melting point (°C)	Density (g/cm ³)	$\Delta G_{298^\circ\text{K}}$ (kJ/mol)	$K_{298^\circ\text{K}}$	$\Delta G_{1000^\circ\text{K}}$ (kJ/mol)	$K_{1000^\circ\text{K}}$
Al	AlH ₃	—	—	+15.5	1.89×10^{-3}	+61	6.24×10^{-4}
Mg	MgH ₂	—	—	-17.9	1.4×10^3	+28.4	0.032
Si	{SiH ₄ }	-185	Gas	-1.9	2.13	+11.4	0.25
Sr	SrH ₂	675	3.72	-70.1	2×10^{12}	-23.4	16.8
Na	NaH	800	0.92	-33.6	7.85×10^5	+20.3	0.087
Ca	CaH ₂	816	1.9	-73.7	8.39×10^{12}	-27.9	28.8

equilibrium constant for the reactions of formation of different hydrides at 298°K (25°C). According to Table II the elements such as calcium, strontium and sodium have a high propensity to compose the hydride compounds at the ambient temperature. In addition, according to the stability temperature of the hydroxide compound in Table III the elements such as Na, Sr, Ca and Mg have stable hydroxides at the ambient temperature. Therefore, similar to the experimental studies of Gruzleski *et al.* [13] the thermodynamically evaluations show that the surfaces of strontium and strontium master alloys will be covered with SrH₂ and Sr(OH)₂ if they are held long time at ambient condition and hydrogen will enter the aluminium melt through Sr-modification treatment. In spite of above conclusion the results of Figs 1 and 2 show that Sr-addition cannot increase the hydrogen content of the melt directly. They also confirm that the content of Sr(OH)₂ and SrH₂ which can probably enter the melt through addition of Al-10%Sr master alloy can not increase the hydrogen content of the melt considerably. Two possible explanations can be expressed. It is probable that the content of hydrogen containing compounds, which enter the melt through Sr-addition, is not in sufficient quantity to increase the hydrogen content of the melt noticeably. A second explanation results to the thermochemical properties in Tables II and III which indicates that the suspended compounds of SrH₂ and Sr(OH)₂ can be stable in the Sr-modified Al-Si melts and can not be taken into account by hydrogen measurement techniques. The negative free energy of formation of SrH₂ at 1000°K (Table II) shows that this compound has a high stability even at the temperatures range of Al-Si melts. It is also seen that Sr(OH)₂ can remain stable at the temperature range of Al-Si melts (Table III). Other investigators [10, 11, 15] have also reported the presence of SrH₂ and hydrogen containing SrO in Al-Si melts. Despite the above hypotheses, in order to evaluate precisely the stability of hydrides and hydroxides of modifier elements in Al-Si melts, the formation of SrH₂ and NaOH which is the most stable

TABLE III Thermochemical properties of different hydroxides [24, 25]

Element	Hydroxide	Stability Temps (°C)	Density (g/cm ³)
Al	Al(OH) ₃	<150	2.24
Mg	Mg(OH) ₂	<350	2.36
Sr	Sr(OH) ₂	<710	3.62
Na	NaOH	<1390	2.13
Ca	Ca(OH) ₂	<580	2.24

hydroxide compounds at the temperature range of Al-Si melts, is studied below.

3.1. Thermodynamic study of formation of SrH₂ in Al-Si melts

SrH₂ in Al-Si melt can be formed by equation below:



$$K = \frac{[a_{\text{SrH}_2}]}{[\text{wt}\% \text{Sr}][\text{wt}\% \text{H}]^2} \quad (2)$$

Where K is equilibrium constant of reaction (1), $[a_{\text{SrH}_2}]$ is the activity of SrH₂ in the melt and $[\text{wt}\% \text{Sr}]$ and $[\text{wt}\% \text{H}]$ are the weight percent of dissolved strontium and hydrogen in the melt. Since a suspended particle of SrH₂ is an independent compound in Al-Si melts, therefore $[a_{\text{SrH}_2}] = 1$. The concentration of dissolved Sr in modified Al-Si melts is generally about 0.02 wt% and the concentration of dissolved hydrogen in not degassed Al-Si melts is about 0.3 cc/100 g, Al (0.25 ppm or 2.5×10^{-5} wt%). Considering Equation 2 and contents of strontium and hydrogen the equilibrium constant for reaction (1) will be 8×10^{10} . So if the right hand side of Equation 2 becomes higher than 8×10^{10} , SrH₂ becomes a stable compound in Al-Si melts and can be formed and if the RHS of Equation 2 becomes lower than 8×10^{10} , SrH₂ is not stable and will dissociate to $[\text{Sr}]$ and $[\text{H}]$ dissolved in the melt. The below equation shows the Gibbs free energy for Equation 1.

$$\Delta G = -70005 + 57.654 T - 1.987 T \text{Ln}(\gamma_{\text{Sr}}), \quad (3)$$

Cal/mol [24, 26]

Where γ_{Sr} is the activity coefficient of dissolution of Sr in liquid Al-Si and ΔG is the Gibbs free energy of reaction of dissolved Sr and H in Al-Si melt to form $\langle \text{SrH}_2 \rangle$ in weight percent standard. The equilibrium constant for Equation 1 can be calculated as below:

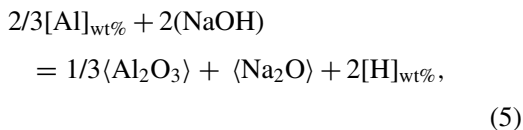
$$K = \exp(-\Delta G/RT) \quad (4)$$

By considering the Equations 3 and 4, it can be concluded that $\langle \text{SrH}_2 \rangle$ is stable in Al-Si melt when γ_{Sr} becomes greater than 1.598×10^8 ($K_{1000^\circ\text{K}}$ becomes higher than 8×10^{10}). Although γ_{Sr} in Al-Si alloys has not been determined, but by considering the information below about dissolution of Sr in Al-Si solution, it can be evaluated that γ_{Sr} in Al-Si melt should be significantly small.

- a. The solubility of Sr in solid aluminium is almost zero [27].
- b. Dissolution of Sr in aluminium is strongly exothermic [1].
- c. The phase diagram of Al-Si-Sr [27] show that the dissolution of Sr in Al-Si melts is accompanied with the formation of different intermetallic compounds having high melting point such as Al_4Sr , Al_2Sr , $SrSi_2$, $SrSi$ and different compounds of $AlSiSr$. In such a case γ_{Sr} is significantly lower than unity ($\gamma_{Sr} \ll 1$) and by considering the Equations 3 and 4 it is concluded that $K_{1000^\circ K}$ is extremely lower than 8×10^{10} . Therefore SrH_2 is an unstable compound in Al-Si melts and can not be formed during and after Sr-modification treatment. By doing similar thermodynamic calculations, it is possible to evaluate that the hydrides of other modifier elements such as NaH and CaH_2 are also unstable compounds in Al-Si melts.

3.2. Thermodynamic study of stability of hydroxide of modifiers in Al-Si melts

According to Table III, $Sr(OH)_2$ is stable at the temperatures below $710^\circ C$ ($983^\circ K$) in normal atmospheric conditions. If $Sr(OH)_2$ exists in Sr-modified Al-Si melts at temperatures higher than $710^\circ C$ ($983^\circ K$), it will be decomposed to SrO and H_2O . It is also seen that NaOH is the most stable hydroxide at $1000^\circ K$ and it can remain stable at different temperature range in aluminium alloys. In order to determine whether NaOH can be stable in Al-Si melts, its reactivity with aluminium and other alloying elements should be considered. The stability of free NaOH in aluminium melt can be studied through reaction below:



$$\Delta G_{1000^\circ K} = -137 \text{ kJ/mol}, [24]$$

and so $K_{1000^\circ K} = 1.55 \times 10^7$ (6)

The Equations 5 and 6 show that NaOH can not be a stable compound in aluminium melt and if this compound enters into the aluminium melt through Na-modification treatment, it will be decomposed and will release hydrogen to the melt. Besides aluminium, in Sr-modified Al-Si melts, there are other alloying elements such as Mg, Si and Sr, which can react with NaOH and decompose this compound. Since NaOH is the most stable hydroxide compound probable in Al-Si melts, by doing similar thermodynamic calculations it can be concluded that the other hydroxide compounds particularly, $Sr(OH)_2$ can not remain stable in Al-Si melts.

The thermodynamic studies show that all the hydrogen containing compounds of modifier elements are unstable in Al-Si melt and if these compounds enter into the melt they will be decomposed to release hydrogen. Therefore, in order to explain the negligible increase of hydrogen content after Sr-addition in Figs 1

and 2, it can be concluded that the content of SrH_2 and $Sr(OH)_2$ that are introduced to the melt through the Sr-addition is not sufficient to increase the hydrogen content of the melt noticeably. Figs 1 and 2 indicate that, there is no noticeable increase in hydrogen content of the melt after modification. It confirms that Sr-modification cannot increase the rate of hydrogen absorption. This conclusion cannot confirm this hypothesis that Sr-modification should increase the rate of hydrogen absorption by increasing in oxidation rate (reaction with H_2O) or by changing the surface protectivity of oxide layer.

In Fig. 3 the hydrogen content of cleaned and uncleaned melts are compared for unmodified and Sr-modified alloys at $735^\circ C$. For both unmodified and Sr-modified melts, the hydrogen content is higher when samples are taken from melt containing surface oxide layers and it is more pronounced in Sr-modified melt. Fig. 4 shows the results of similar experiment done at $685^\circ C$. It can be seen that the difference between hydrogen content of cleaned and uncleaned melts is not significant in unmodified melts, whereas it is significant in Sr-modified melts, respectively. The general trend of results shows that hydrogen content was higher in the melts containing surface oxide layer. This is because the rate of hydrogen extraction is limited by nucleation of bubbles, and the rate of diffusion to the surface. Melts that are less clean will be expected

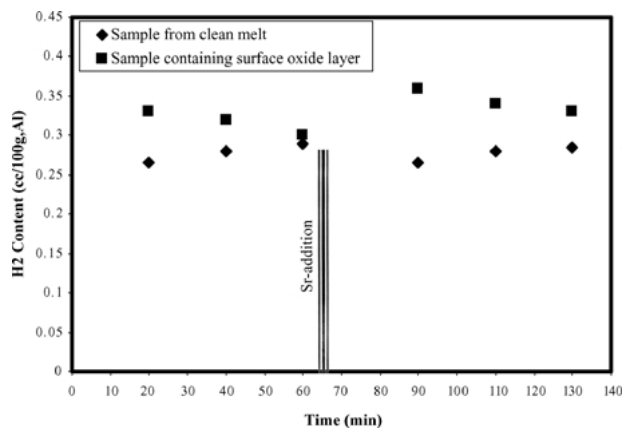


Figure 3 Variation of hydrogen contents vs. holding time before and after Sr-addition in cleaned and uncleaned melts at $735^\circ C$.

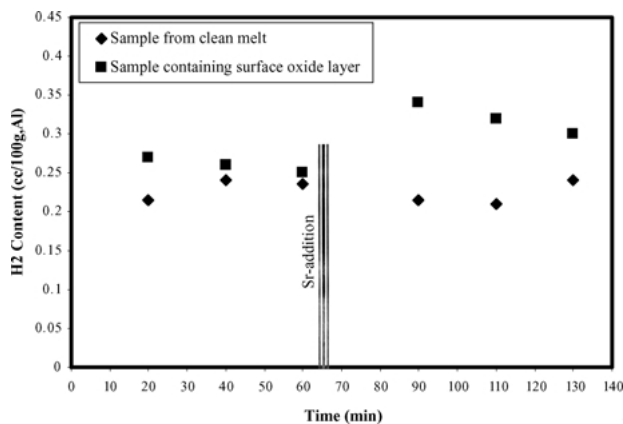


Figure 4 Variation of hydrogen contents vs. holding time before and after Sr-addition in cleaned and uncleaned melts at $685^\circ C$.

to release their hydrogen more quickly and more completely, thus appearing to increase the content of hydrogen in the melt. The existence of oxide layers in the castings is generally accompanied with air, which is entrained within them [28]. Therefore the entrained air between oxide layers can be released under high order of vacuum in HYSCAN instrument and increase the hydrogen content of uncleaned melt. The other reason for higher hydrogen content of uncleaned melts in Sr-modified alloys is related to the existence of a considerable SrO content in the surface oxide layer. It is because strontium was added to the melt surface without any plunging. The scanning electron microscope

observation (Figs 5 and 6) shows some areas of SrO in the surface oxide layer of Sr-modified samples at 685°C and 735°C. On the other hand, the surface oxide layers in unmodified samples consist only of Al₂O₃ and MgO (Fig. 7). As it is explained in Section 3.2, SrO can change to Sr(OH)₂ at the temperatures below 710°C. However Sr(OH)₂ can not remain stable in Al-Si melts even at the temperatures below 710°C, but Sr(OH)₂ may be formed out of melt and on the surface oxide layer and remain in equilibrium with the melt and humid atmosphere, particularly at 685°C. Therefore it is possible that in the samples containing surface oxide layers, Sr(OH)₂ was entrained into the

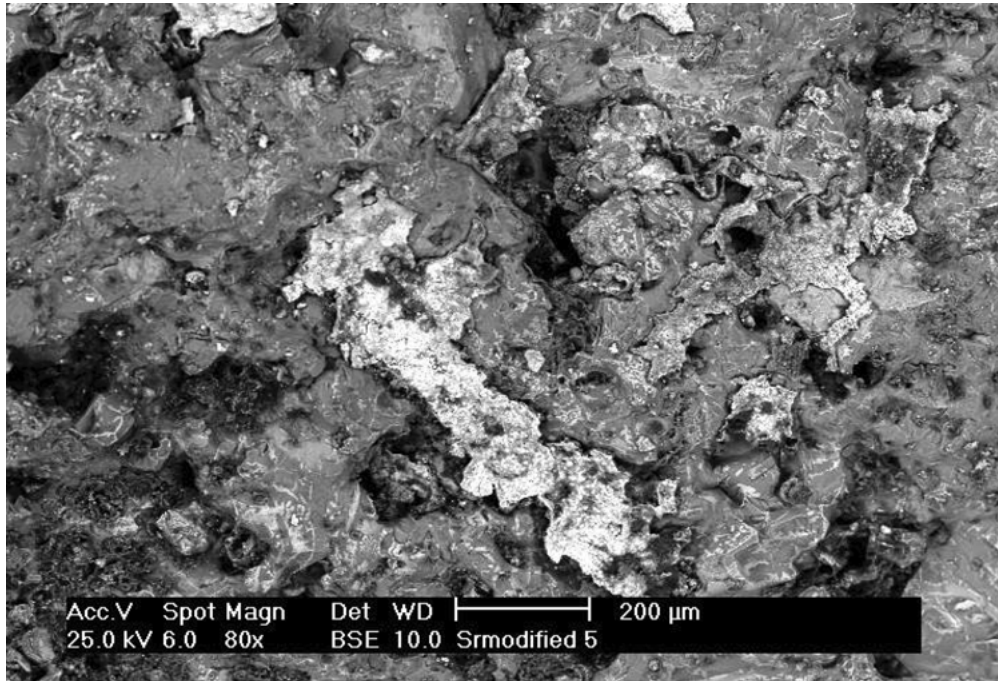


Figure 5 SEM image of typical surface oxide layer of Sr-modified melt at 685°C (White areas are SrO containing oxide and grey areas are Al₂O₃).

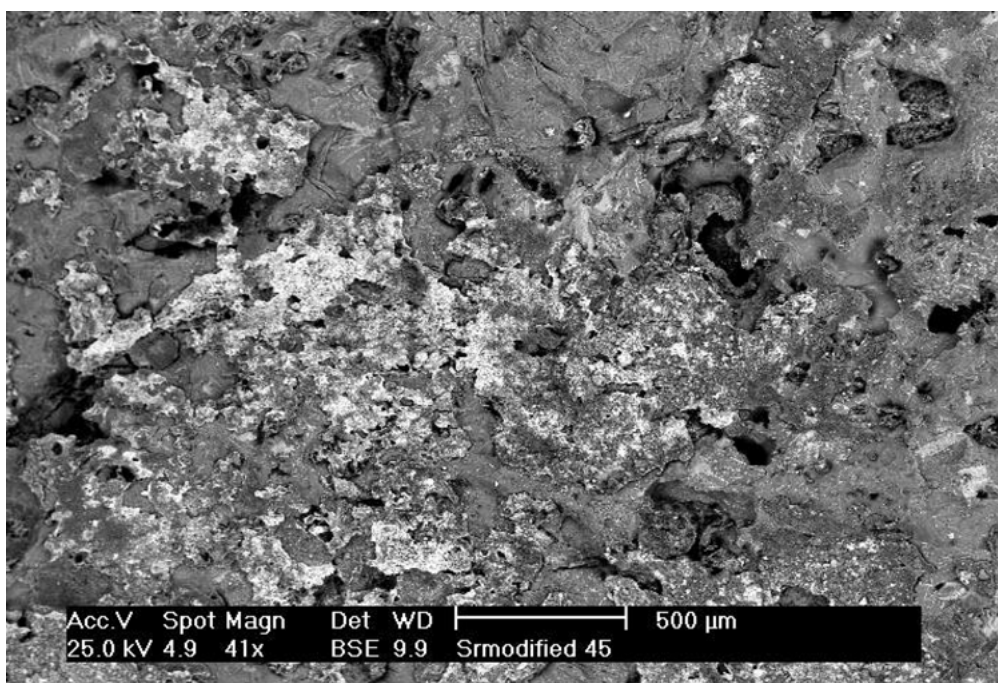


Figure 6 SEM image of typical surface oxide layer of Sr-modified melt at 735°C (White areas are SrO containing oxide and grey areas are Al₂O₃).

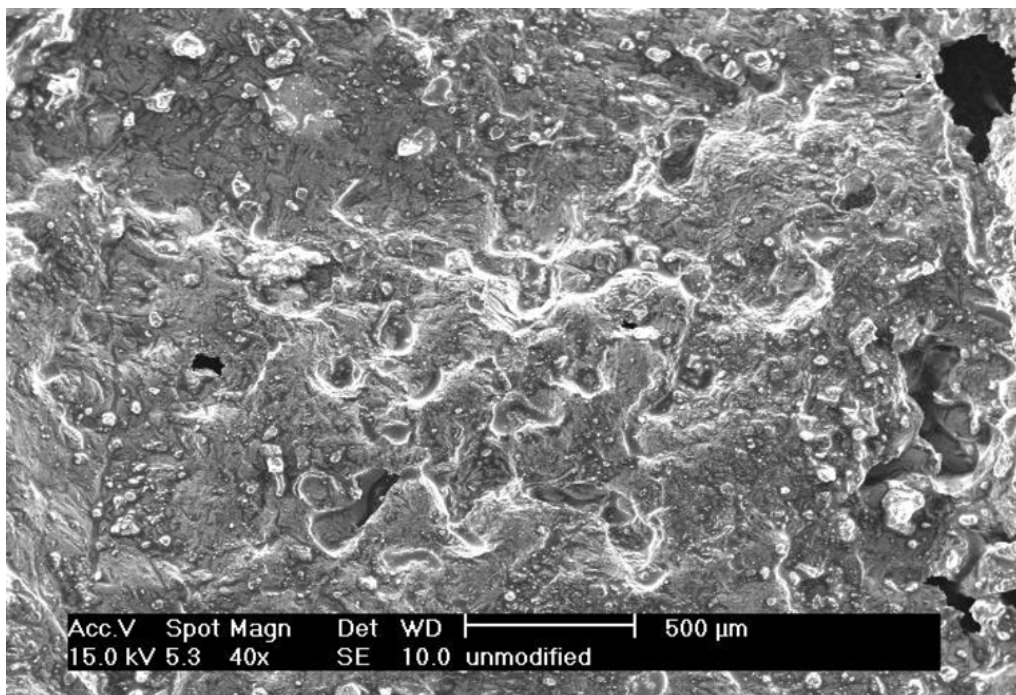


Figure 7 SEM image of typical $\text{Al}_2\text{O}_3 \cdot \text{MgO}$ films in the unmodified melt surface layer at 735°C .

melt and then was decomposed during hydrogen measurement in the HYSCAN instrument.

The other conclusions drawn from the experiments is that when samples were taken from cleaned melt, the hydrogen content of the melt in the first samples after Sr-modification, were slightly decreased and then increased in other samples with time. This trend is also seen for unmodified melts (Figs 1 and 2). But when samples were taken from uncleaned melt for both modified and unmodified melts, hydrogen contents were higher in the first samples and then decreased with time in other samples (Figs 3 and 4). It is because that the content of surface oxide layer were considerable in the first samples. The oxide layers were progressively removed so that its content was decreased from sample to sample. Therefore, the hydrogen content was decreased with time. This change was more considerable for Sr-modified melt at 685°C . Therefore, it can be concluded that the hydrogen content measurement by HYSCAN technique is strongly dependant on the melt cleanliness and melt sampling procedure.

4. Conclusions

1. The melt cleanliness has a significant effect on the result of hydrogen content measurement. The hydrogen content of uncleaned melts (melts containing surface oxide layer) is strongly higher than hydrogen content of cleaned melts.

2. Strontium modification has no marked effect on hydrogen absorption at 685°C and 735°C .

3. Based on scanning electron microscopic (SEM) observations, the surface oxide layers in Sr-modified melts are contained of strontium oxides when strontium is added into melt without plunging.

4. Strontium modification increases the hydrogen content of uncleaned melts (melts containing surface

oxide layers). It is more pronounced at temperatures lower than 710°C .

5. Based on thermodynamic calculations there is no hydrogen containing compounds such as hydrides and hydroxides of modifier elements, which can be stable in aluminium melts.

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