SOLID ELECTROLYTE BASED SENSORS FOR USE IN PROCESSING MOLTEN ALUMINUM

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Electrochemical sensors provide information about the chemical composition of molten metals that can be used to improve control of various metallurgical processes. The most successful and widely used example of such sensors is the oxygen sensor used in steelmaking. This success has led to the development of chemical sensors for improvement of the process efficiency and / or product quality in the aluminum industry.

Dissolved hydrogen from the reaction of molten aluminum with water vapor in the atmosphere can lead to porosity in cast products, so the melt must be degassed prior to casting. Control of the degassing process can be improved with real-time feedback provided by *in situ* measurement of the dissolved hydrogen content. Chemical sensors can also be used to improve control of the alloy composition, which can affect the resulting microstructure. Real-time monitoring of the alloy composition is particularly important for elements that are more volatile or more active than aluminum and thus may be preferentially lost by vaporization or oxidation during processing. Three such elements are sodium, strontium and lithium. Sodium and strontium are added in small amounts to control the microstructure, while lithium is used to produce low-density high-stiffness alloys. Another need for chemical sensors is during reclamation of aluminum scrap, where a magnesium sensor can lead to improved efficiency and reduced emissions associated with removal of magnesium.

The most commonly used solid electrolytes are metal oxides. While many metal-oxide electrolytes conduct oxide-ions, there also are metal-oxide electrolytes that conduct other ions, such as protons and metal ions. The most common oxide-ion conducting electrolyte is stabilized zirconia, which has been used in a hydrogen sensor for molten aluminum (1,2). However, proton-conducting oxides, such as $BaCeO_3$ and $CaZrO_3$ and modified NASICON, are more commonly used for hydrogen sensors (3-7). One of the most widely used solid electrolytes in sensors for molten aluminum is β-alumina. The most direct use of β-alumina, which conducts sodium ions, is for a sodium sensor (8-10). However, β-alumina has also been used in sensors for measuring strontium, lithium and magnesium. In some cases, the β-alumina is ion-exchanged to conduct another ion (*e.g.* Li^+(10,13)), while in other cases the surface is modified to create an auxiliary electrode (*e.g.* Mg (11)). Other oxide electrolytes, such as NASICON (14) and $Li_{3.6}Si_{0.6}P_{0.4}O_4$ (15) have been used to measure alloy composition. Although oxide electrolytes are most common, non-oxide solid electrolytes, such as CaH_2 (16) and various fluorides (LaF_3 (17), SrF_2 (18), and MgF_2 (19)) have also been used. Some examples of solid electrolytes used in sensors for detecting various species in molten aluminum are summarized in Table I. In this paper, progress in the development of solid electrolyte based sensors for use in molten aluminum will be reviewed.

Table I. Solid Electrolytes Used in Sensors for Molten Aluminum

Sensor	Electrolyte	
	Oxide	Non-Oxide
Hydrogen	Zirconia (1,2)	CaH_2 (16)
	$BaCeO_3$ (3)	
	$CaZrO_3$ (4,5)	
	NASICON (6,7)	
Sodium	β-alumina (8-10)	LaF_3 (17)
	NASICON (14)	
Strontium	β-alumina (11,12)	SrF_2 (18)
Lithium	β-alumina (10,13)	
	$Li_{3.6}Si_{0.6}P_{0.4}O_4$ (15)	
Magnesium	β-alumina (11)	MgF_2 (19)

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