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# Differential aeration corrosion of silver in sulfate melts at 900 °C

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## Abstract:

The thermodynamic of the  $Ag/Ag_2SO_4$  electrode, serving as reference for carrying electrochemical experiences of corrosion in sulfates at 900°C, was investigated because of the observed limited operating lifetime. Its use led to the total degradation of the  $\varnothing 1$  mm Ag wire in  $\sim 200$  h. Half-immersion of Ag wires in sulfates mixes (selected for their acido-basicity) evidenced the homogeneous thinning of the immersed part of the wires and the precipitation of metallic Ag in the salt. The different steps governing the corrosion mechanism were proposed considering that the driving force was the differential aeration of the Ag wire.

**Keywords:** A. Silver, C. Hot corrosion, A. Molten salts

## Main text

Performing electrochemical measurements is an appropriate approach to investigate hot corrosion of metals and alloys in molten salts. Indeed, these techniques allow the *in situ* determination of many kinetic and thermodynamic parameters that are impossible to acquire otherwise. For example, it is possible to monitor the evolution of the open circuit potential *vs* time of a metallic material [1,2], to evaluate its passivation ability, or to acquire significant information about the nature of the electro-active systems [1,3-7] that are present in the electrolytic melt, this list being by far non-exhaustive.

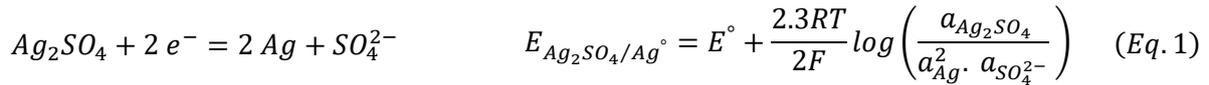
Many researchers developed three electrodes cells, employing refractory ceramic and metallic materials, capable to withstand the high temperature required for operating in refractory salts [8,9] [10] or oxides mixes [11]. Rapp *et al.* [12,13] matured this technique in the past to investigate the electrochemical reactions in a pure  $Na_2SO_4$  melt because of the need to understand the mechanism of hot corrosion of alloys in molten sulfates. Indeed, the severe degradation observed on aero-engines hardware after operations [14] is a long-term technological issue, while the temperature of the aeronautic turbines is continuously increasing in order to enhance their efficiency. The authors [12] developed electrodes systems to record, sometimes simultaneously, the oxide ions activity ( $a_{O^{2-}}$ ), the partial pressure of oxygen ( $P_{O_2}$ ) and the open circuit potential of nickel leading, for example, to the identification of its corrosion mechanism [15].

For these measurements, a suitable reference has to be selected. Rapp *et al.* published [16] a series of electrodes that can be used in molten sulfates, and the  $Ag/Ag_2SO_4$  reference electrode is generally recommended due to its relative building simplicity [9,17].

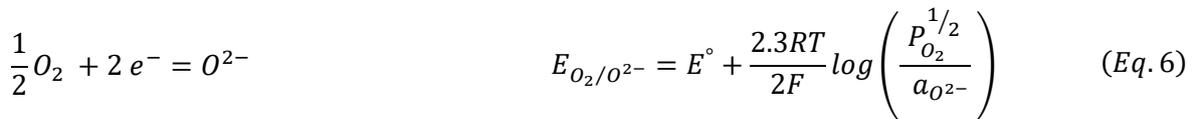
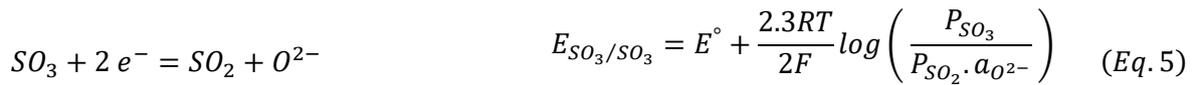
Because of a number of experimental issues met by the present authors when performing more or less long-term experiments (between 50 h and 200 h) in molten sulfates with this electrode, the thermodynamic of the  $Ag/Ag_2SO_4$  reference electrode was re-investigated, as well as the behavior of metallic  $Ag$  in  $Na_2SO_4$  and  $Ag_2SO_4 - Na_2SO_4$  mixture. These results are discussed and mechanisms are proposed in the present short communication.

The  $Ag/Ag_2SO_4$  reference electrode consists of a silver wire dipped into a 10 mol.%  $Ag_2SO_4 - Na_2SO_4$  salt mixture confined in a mullite ( $3Al_2O_3 - 2SiO_2$ ) tube. The glassy phase at grain boundaries in mullite provides the mandatory ionic conduction, by  $Na^+$  ions in this case [9]. The half-cell corresponding to the  $Ag/Ag_2SO_4$  reference electrode and the corresponding Nernst Equation (Eq.1) can be written as follows:

Half Cell :  $Ag$  wire, 10 mol.%  $Ag_2SO_4 - Na_2SO_4$  | Mullite ( $Na^+$ ) | Molten salt to be studied



The different chemical reactions that have to be considered in this system are listed below:



The use of this electrode as a reference for electrochemical measurements supposes that:

- the mullite conductivity is high enough to avoid the formation of a membrane potential,
- the thermal stability of the constitutive salts, i.e., of  $Na_2SO_4$  and  $Ag_2SO_4$  compounds, is ensured at the temperature of use,
- the concentration of silver ions remains constant with time; i.e., that the mullite is impermeable to  $Ag^+$  ions at  $900^\circ C$ .

Thermogravimetry was employed to evaluate the thermal stability of  $Na_2SO_4$ ,  $Ag_2SO_4$  and of the 10 mol.%  $Ag_2SO_4 - Na_2SO_4$  mixture in air. The thermal decomposition of  $Na_2SO_4$  in air (Fig.1a) was

observed to start from 850°C and occurred with a very low reaction rate at 900°C. To confirm that the  $Na_2SO_4$  decomposition can be neglected at 900°C, an amount of  $11.48 \pm 0.01$  milligrams  $Na_2SO_4$  was exposed during 100 h at 900°C in still air. The mass loss after exposure corresponded to 5.05% of the initial weight. The residue was then solubilized in 0.5 ml of fresh distilled water and the pH was assessed using a pH indicator strip. This dilution procedure was implemented regarding the low mass variation after 100 h and assuming that the mass loss resulted from the decomposition of  $Na_2SO_4$  according to Eq.2. The calculation of the pH resulting from  $SO_3$  release led to  $pH > 12$ . Such pH variation from the one of distilled water (around 7) should have been observed, but the color of the strip was identical to the one dipped in pure distilled water, confirming first that if any, the decomposition of the salt according to Eq.2 is very low, and second that the mass loss should rather be associated to  $Na_2SO_4$  (g) loss than to its decomposition.

At the opposite, the mass loss was rapid for pure  $Ag_2SO_4$  (Fig.1b) and reached 31.2% of the initial weight of  $Ag_2SO_4$  after only 2 hours at 900°C. This value corresponds to the total decomposition of  $Ag_2SO_4$  in air according to Eq.3. In the case of the 10 mol. %  $Ag_2SO_4 - Na_2SO_4$  mixture (Fig.1c), and if the decomposition of  $Na_2SO_4$  is neglected, 90% of  $Ag_2SO_4$  has decomposed after 24 h at 900°C.

*Fig.1: Mass change vs time of a)  $Na_2SO_4$ , b)  $Ag_2SO_4$  and of c) the 10 mol. %  $Ag_2SO_4 - Na_2SO_4$  mixture in air at 900°C (heating rate of 20 K.min<sup>-1</sup> and gas flow rate of 20 ml.min<sup>-1</sup>)*

According to these results,  $Ag_2SO_4$  rapidly decomposed in air despite the positive Gibbs energy related to Eq.3. This is due, of course, to the impossibility to reach thermodynamic equilibrium in an open system,  $SO_3$  being promptly evacuated. Consequently, the mullite tube confining the salt mixture of the  $Ag/Ag_2SO_4$  reference electrode has to be sealed to limit the  $Ag_2SO_4$  decomposition reaction.

If the mullite tube is now assumed to be sealed, reaching equilibrium 3 inside the mullite tube nevertheless requires a slight decomposition of  $Ag_2SO_4$ ; the involved amount is evaluated now. Considering a unit activity of  $Ag_2SO_4$ , the  $SO_3$  partial pressure at 900°C in air (0.21 atm  $O_2$ ) resulting from Eq.3 should be as high as  $1.74 \cdot 10^{-3}$  atm. As the  $SO_3$  partial pressure in air at 900°C is related to the ones of  $SO_2$  and  $O_2$  through Eq.4, the  $SO_2$  partial pressure can be calculated. At 900°C, the value of  $SO_2$  partial pressure at equilibrium is more than thirty-fold the one of  $SO_3$ . Thus, the amount of  $Ag_2SO_4$  that has to decompose to reach equilibrium in the mullite tube can be calculated. This amount, for 1 grams of the 10 mol. %  $Ag_2SO_4 - Na_2SO_4$  mixture introduced in a 10 cm<sup>3</sup> mullite tube, and assuming neither  $SO_3$  nor  $SO_2$  condense on the colder upper part of the system, does not exceed 1% of the initial  $Ag_2SO_4$ . Taking into account an activity of  $Ag_2SO_4$  in the melt equal to 0.1, i.e., considering the solution as ideal, the initial amount of  $Ag_2SO_4$  initially consumed falls at 0.1%. These considerations suggest that the mullite tube constituting the  $Ag/Ag_2SO_4$  reference electrode must be efficiently sealed to limit the  $Ag_2SO_4$  decomposition, but also that the sulfate mixes should be chemically stable once the equilibrium

in the tube is achieved. Thus the  $Ag_2SO_4$  activity is fixed, and the  $Ag/Ag_2SO_4$  system can be used as reference potential.

However, unpredicted observations were made after the mullite tube broke during the run of a 65 h experiment at 900°C. The  $Ag$  wire, which was initially 1 mm in diameter, exhibited a sponge-like appearance (Fig.2) when immersed in the 10 mol.%  $Ag_2SO_4 - Na_2SO_4$  mixture. Besides, the composition of the residual salt was close to the initial one.

*Fig.2: Broken  $Ag/Ag_2SO_4$  reference electrode after 195 h immersion in  $Na_2SO_4$  at 900°C. The photo displays the  $Ag$  sponge formed in place of the initially 1 mm in diameter  $Ag$  wire.*

In order to understand this phenomenon, three  $Ag$  wires ( $\varnothing$  1 mm) were immersed in pure  $Na_2SO_4$ , 10 mol.%  $Ag_2SO_4 - Na_2SO_4$  and 10 mol.%  $Ag_2SO_4 - 56 - 44$  mol.%  $Na_2SO_4 - MgSO_4$  respectively, this latter being under consideration to carry out electrochemistry in molten sulfates at 700°C, the melting temperature of the eutectic composition (56 - 44 mol.%  $Na_2SO_4 - MgSO_4$ ) [21,22] being at 670°C.

The macroscopic views of the wires after the 96 h exposure at 900°C in air are given in Fig.3. No reaction was observed for the  $Ag$  wire immersed in pure  $Na_2SO_4$ , whereas the diameter of the wires immersed in the two  $Ag_2SO_4$  containing melts rapidly decreased in comparison to the external part of the  $Ag$  wire. Moreover metallic  $Ag$  particles were observed widespread in the melt after exposure and the salt mixes still contained  $Ag_2SO_4$  after the 96 h exposure in air. These observations were initially considered as really amazing, with the question of what can be the driving force leading to the oxidation of  $Ag$  wire and then to its re-formation as dispersed  $Ag$  particles in the melt, i.e. with the same chemical potential. Moreover the thermogravimetric study presented hereabove evidenced the almost total decomposition of  $Ag_2SO_4$  after 24 h at 900°C.

*Fig.3: Macroscopic views of  $Ag$  wires partly immersed in a)  $Na_2SO_4$ , b) 10 mol.%  $Ag_2SO_4 - Na_2SO_4$  and c) 10 - 56 - 44 mol.%  $Ag_2SO_4 - Na_2SO_4 - MgSO_4$  molten salts for 96 h at 900°C in air. The black arrows indicate the limit between the immersed and outer parts of the  $Ag$  wire*

All the results suggest in fact the fast oxidation of the  $Ag$  wire occurs by a differential aeration corrosion phenomenon. Differential aeration corrosion (DAC) is a type of corrosion that occurs when the oxygen concentration (or that of another oxidant present in the surrounding environment) varies along a metal's surface [23]. The gradient of concentration of oxidants creates a difference in potential on the metal's surface such that electronic transport through the metallic conductor can occur, resulting in the formation of anodic and cathodic sites. In the present case, because  $O_2(g)$  and  $SO_3(g)$  are the main oxidants in the environment and their solubilities into molten sulfates were low [24], the direct oxidation of  $Ag$  by these solvated oxidants is in fact not expected. If the oxidants were present into the melt, their consumption would lead to an increase of the concentration of oxide ions  $O^{2-}$ , i.e., of the basicity of the

melt, according to the Eq.5 and Eq.6, and thus to the stabilization of metallic  $Ag$  according to the Kellogg diagrams (Fig.4) of the  $Ag$  system in the presence of sulfate ions.

*Fig.4: Kellogg diagram of the Na and Ag systems in presence of sulfate ions, drawn at 900°C with activity of the ionic species  $Na^+$  and  $Ag^+$  equal to 1 and 0.1 resp. [25,26]*

The Kellogg diagram indicates the predominant species as a function of the partial pressures of both oxygen ( $P_{O_2}$  in ordinates) and  $SO_3$  ( $P_{SO_3}$  in abscissa). For systems involving oxide ions, it is convenient to use the  $pO^{2-}$ -notation (Eq.8) that traduces the activity of  $Na_2O$ , itself related to the partial pressure  $P_{SO_3}$  by Eq.2. A high  $pO^{2-}$  value corresponds to an acidic environment (to high  $P_{SO_3}$  value on the Kellogg); a low  $pO^{2-}$ , to a basic one (to low  $P_{SO_3}$  value resp.). The activity of an ionic compound such as  $Na_2O$  is given by the  $(a_{Na^+})^2 \cdot a_{O^{2-}}$  [27] product. Considering molten salts as ionic solutions and making the assumption of the ideal mixture, the activity of  $Na^+$  is equal to unity (from [28]). Therefore the activity, or concentration, of  $O^{2-}$  is equal to the activity of  $Na_2O$  in the salt.

$$pO^{2-} = -\log[a_{Na_2O}] = -\log[a_{O^{2-}}] \quad (Eq. 8)$$

Thus the DAC mechanism, sketched in Fig.5, can be proposed:

- The cathodic, and kinetically determining, reactions correspond to the reduction of  $O_2$ , or/and  $SO_3$  when present, according to Eq.5 and 6 respectively. Both reactions occur on the  $Ag$  wire in the outer region where the salt spreads by capillary action over the  $Ag$  wire, as indicated in the figure 5. Oxygen from the gaseous atmosphere can easily diffuse through this thin film of  $Na_2SO_4$  and then reacts with electrons to form  $O^{2-}$  ions. Consecutively the concentration of oxide ions in the upper region of the melt increases. Considering the oxide ions concentration equal to the  $Na_2O$  activity, equilibrium 2 suggests the decrease of  $P_{SO_3}$  in this region.  $Ag_2SO_4$  in this low  $P_{SO_3}$  region decomposes to form  $SO_3$ ,  $O_2$  and  $Ag^\circ$  according to the Kellogg diagram (fig. 4). The gaseous species ( $SO_3$ ,  $O_2$ ) are rapidly released in the gas phase because of their low solubility in the molten salt [29].
- The anodic reaction, *i.e.* the oxidation of the  $Ag^\circ$  wire, occurs in the immersed part where the conditions of acidity allow the formation of  $Ag_2SO_4$ , as planned from the known thermodynamic data of pure substances (Fig.4). The formation of  $Ag^+$  through this oxidation maintains the required acidity of the melt.
- The difference of  $Ag^+$  concentration between the immersed zone and the upper region surrounding the silver wire involves a constant flow of  $Ag_2SO_4$  ( $J_{Ag^+}$ ) towards the cathodic site where it decomposes into small-sized particles of  $Ag$  where the  $pO^{2-}$  is low enough.

*Fig.5: Sketches of a) the differential aeration corrosion settling between the anodic (A) immersed and cathodic (C) emerged parts of the Ag wire; b) the current-potential curves for the involves systems*

according to the acidity of the melt 1)  $Na_2SO_4$ , 2) 10 mol. %  $Ag_2SO_4 - Na_2SO_4$  and 3) 10 – 56 – 44 mol. %  $Ag_2SO_4 - Na_2SO_4 - MgSO_4$ .

According to this sketch, when 2 electrons are involved in the reduction of  $\frac{1}{2} O_2 (g)$  at the cathodic site forming  $O^{2-}$ , 2  $Ag^\circ$  atoms form 2  $Ag^+$  ions at the anodic site, and, somewhere near the cathodic site, 2  $Ag^+$  ions (in  $Ag_2SO_4$ ) precipitate with  $O^{2-}$  to form the instable  $Ag_2SO_4$  (or  $Ag_2O$ ), that decomposes into metallic  $Ag$ . This electron exchange balance shows that the  $Ag_2SO_4$  concentration does not change with time if steady state conditions are considered. This situation is in fact verified until the  $Ag$  wire is totally consumed.

This mechanism similarly occurs in the sealed mullite tube. The oxygen partial pressure is maintained constant through Eq.3 by which oxygen is produced and Eq.6 by which it is consumed. A modification of the gas inside the mullite tube, by using argon instead of air for example, would have a low influence on the differential aeration corrosion. Indeed, this would just increase the amount of  $Ag_2SO_4$  in the 10 mol. %  $Ag_2SO_4 - Na_2SO_4$  mixture that has initially to decompose into  $SO_3 (g)$ ,  $SO_2 (g)$ , and  $O_2 (g)$  to reach equilibrium.

The results also evidence that the differential aeration corrosion did not develop in the case of pure  $Na_2SO_4$  but did with the presence of  $Ag_2SO_4$ , and even more significantly with the  $Ag_2SO_4 - Na_2SO_4 - MgSO_4$  mixture. In the open conditions that are employed for these tests,  $O_2 (g)$  is the main oxidant because it can be assumed that the partial pressure of  $SO_3 (g)$  remains very low and that the gas can be evacuated far from the cathodic site. But no matter the involved redox couple, both similarly evolve with the change of the acidic conditions into the melt, as traduced by the Nernst equations indicated in Eq.5 and 6. In fact, the oxidative strength of both  $O_2 (g)$  and  $SO_3 (g)$  increase when the activity of oxygen ions ( $a_{O^{2-}}$ ) decreases. This allows to classify the electrolytes used in the present study from the less to the more acidic: pure  $Na_2SO_4 < 10 \text{ mol. \% } Ag_2SO_4 - Na_2SO_4 < 10 - 56 - 44 \text{ mol. \% } Ag_2SO_4 - Na_2SO_4 - MgSO_4$ . This effect is sketched in Fig.5b showing the current vs. potential curves shifting on the right with the increase of acidity.

To summarize the observations, the mullite tube has to be carefully sealed to avoid the  $Ag_2SO_4$  decomposition during the use of the  $Ag/Ag_2SO_4$  reference electrode at 900°C. The immersed part of the  $Ag$  wire is consumed with time and its lifetime strongly depends on the acidic character of the molten salt. Nevertheless, the DAC, which is at the origin of this consumption maintains a constant concentration of  $Ag_2SO_4$  in the melt, and thus the  $Ag/Ag_2SO_4$  electrode keeps a constant potential with time until there is no more contact between the  $Ag$  wire and the electrolytic salt. A decrease of the salt acidity by lowering the  $Ag_2SO_4$  concentration or by adding a sulfate to the melt with a more basic character can increase the  $Ag/Ag_2SO_4$  reference electrode lifetime.

Finally, this study supplies wider conclusions since it contributes to evidence the significant effect of the surrounding gaseous atmosphere when performing electrochemical or corrosion tests involving partial immersion of the metallic specimen into the melt. According to the oxidative species contained in the environment and to the solubility of these oxidants in the molten salt, a DAC can settle such that very different chemical conditions can be established at the anodic and cathodic sites. The corrosion behavior in such conditions can be very different from the one observed when a small amount of salt is homogeneously sprayed to form a deposit on the specimen to be tested [30]. Consequently, the total immersion of the electrode in the melt is required when carrying out electrochemistry in general and oxidants should be introduced directly in the melt close to the electrode rather than just flowing over the salt.

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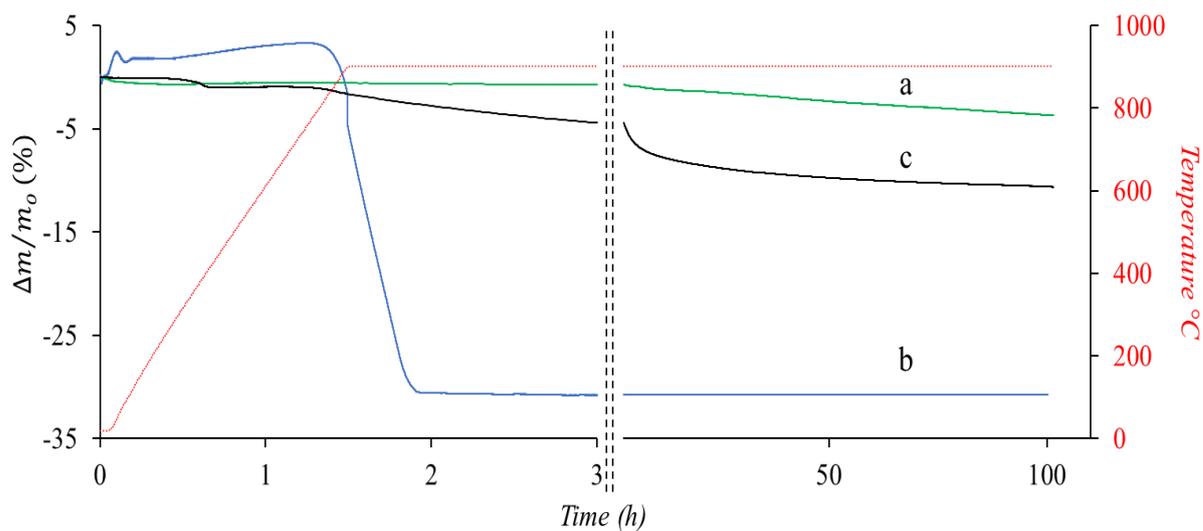
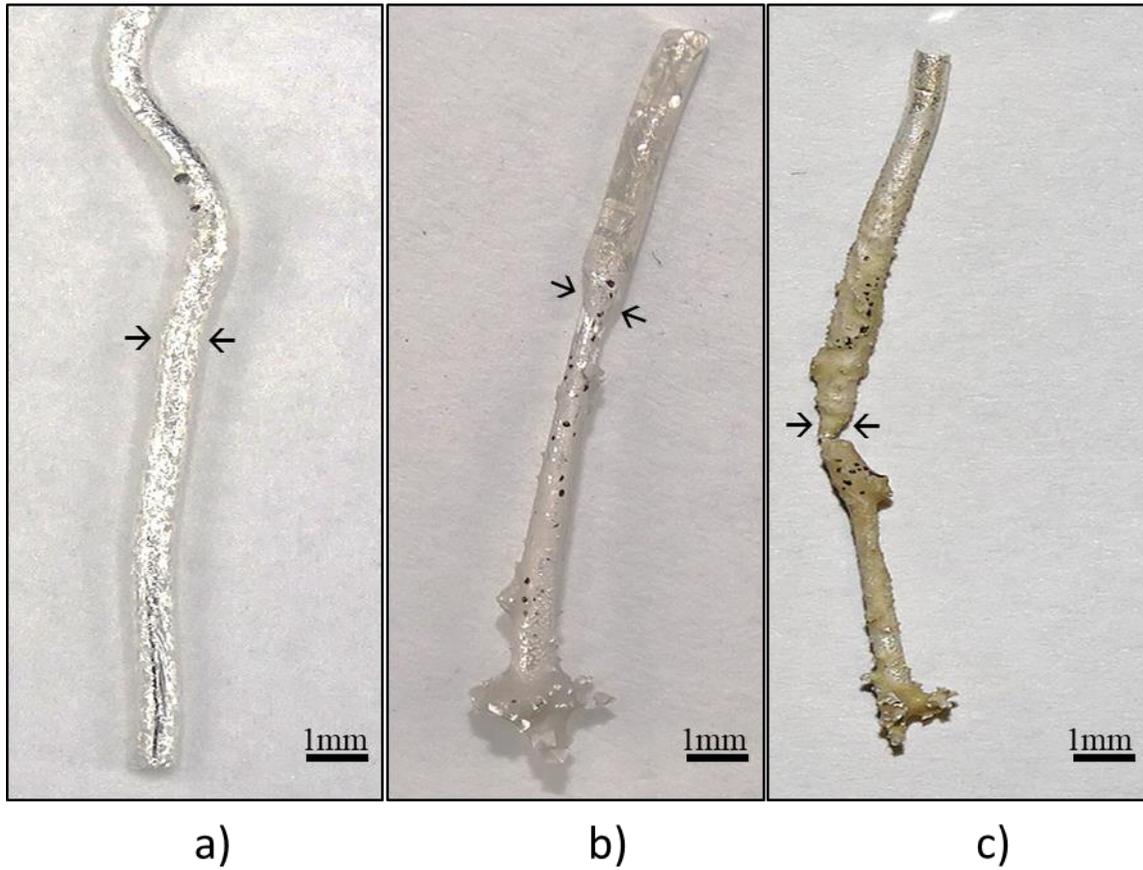


Fig.1: Mass change vs time of a)  $\text{Na}_2\text{SO}_4$ , b)  $\text{Ag}_2\text{SO}_4$  and of c) the 10 mol.%  $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$  mixture in air at  $900^\circ\text{C}$  (heating rate of  $20 \text{ K}\cdot\text{min}^{-1}$  and gas flow rate of  $20 \text{ ml}\cdot\text{min}^{-1}$ )



Fig.2: Broken  $\text{Ag}/\text{Ag}_2\text{SO}_4$  reference electrode after 195 h immersion in  $\text{Na}_2\text{SO}_4$  at  $900^\circ\text{C}$ . The photo displays the Ag sponge formed in place of the initially 1 mm in diameter Ag wire.



*Fig.3: Macroscopic views of Ag wires partly immersed in a)  $\text{Na}_2\text{SO}_4$ , b) 10 mol.%  $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$  and c) 10 - 56 - 44 mol.%  $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{MgSO}_4$  molten salts for 96 h at  $900^\circ\text{C}$  in air. The black arrows indicate the limit between the immersed and outer parts of the Ag wire*

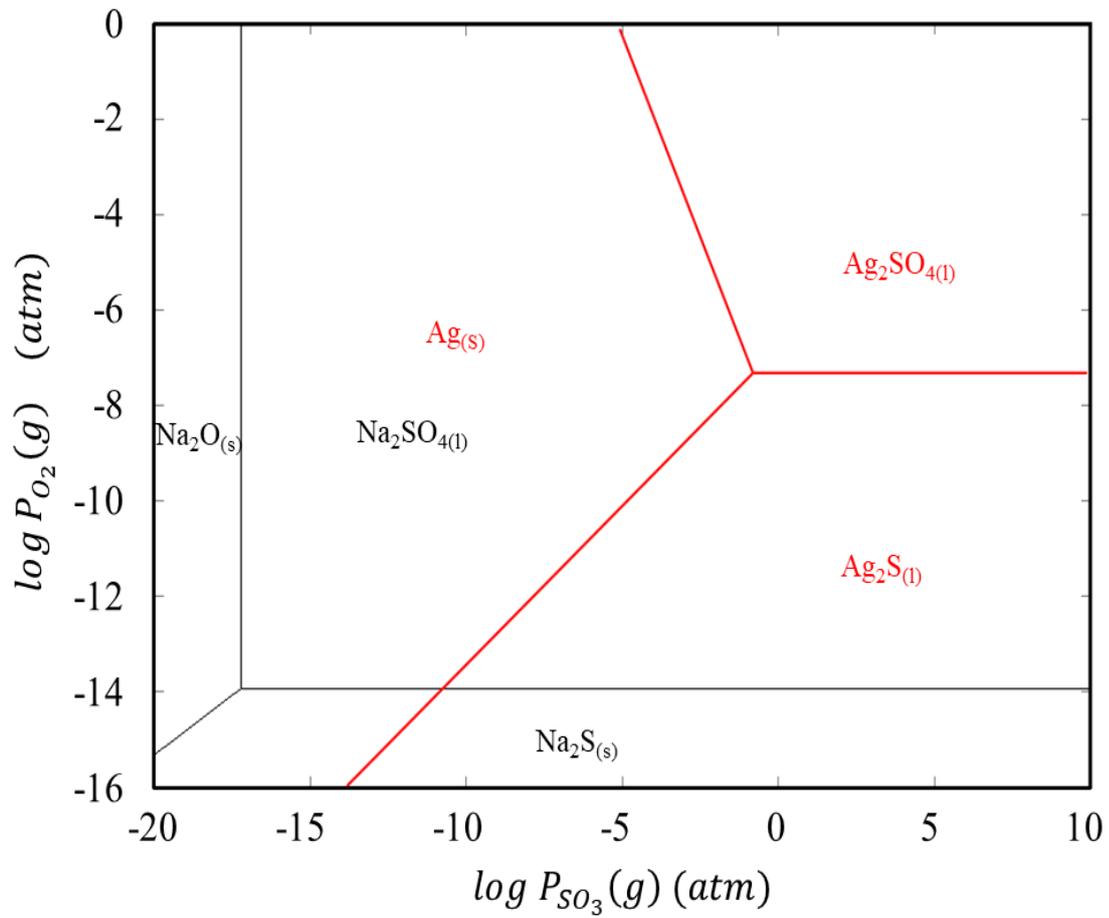


Fig.4: Kellogg diagram of the Na and Ag systems in presence of sulfate ions, drawn at 900°C with activity of the ionic species  $Na^+$  and  $Ag^+$  equal to 1 and 0.1 resp. [15-16]

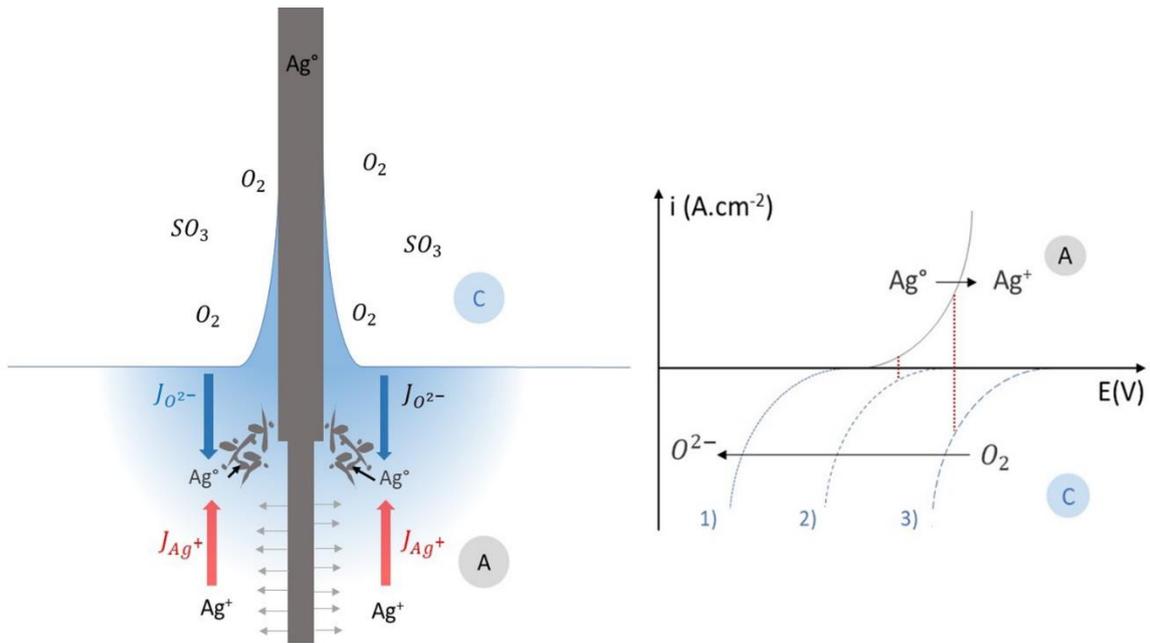


Fig.5: Sketches of a) the differential aeration corrosion settling between the anodic (A) immersed and cathodic (C) emerged parts of the Ag wire; b) the current-potential curves for the involves systems according to the acidity of the melt 1)  $\text{Na}_2\text{SO}_4$ , 2) 10 mol. %  $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$  and 3) 10 - 56 - 44 mol. %  $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{MgSO}_4$ .