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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 ~ 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.

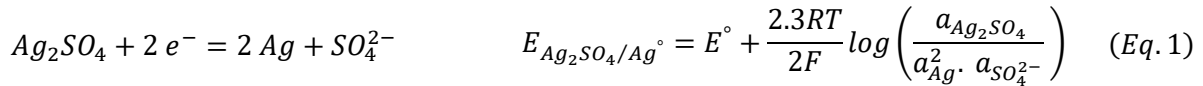
Many researchers developed three electrodes cells, employing refractory ceramic and metallic materials, capable to withstand the high temperature required for operating in refractory salts [8,9] [10] or oxides mixes [11]. Rapp *et al.* [12,13] matured this technique in the past to investigate the electrochemical 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].

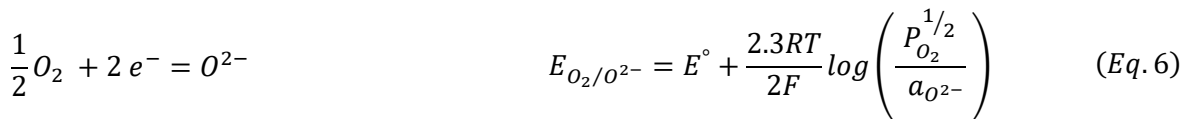
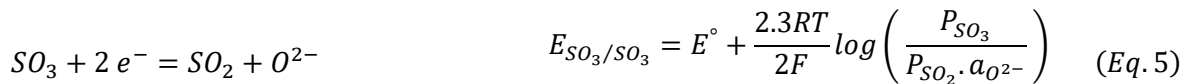
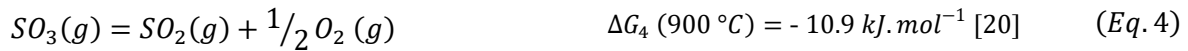
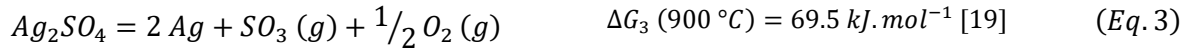
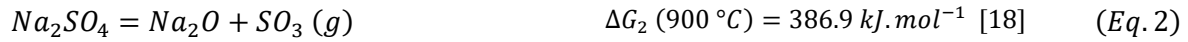
Because of a number of experimental issues met by the present authors when performing more or less long-term experiments (between 50 h and 200 h) in molten sulfates with this electrode, the thermodynamic of the Ag/Ag_2SO_4 reference electrode was re-investigated, as well as the behavior of metallic Ag 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 ± 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⁻¹ and gas flow rate of 20 ml.min⁻¹)

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 cm³ 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° 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° 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° 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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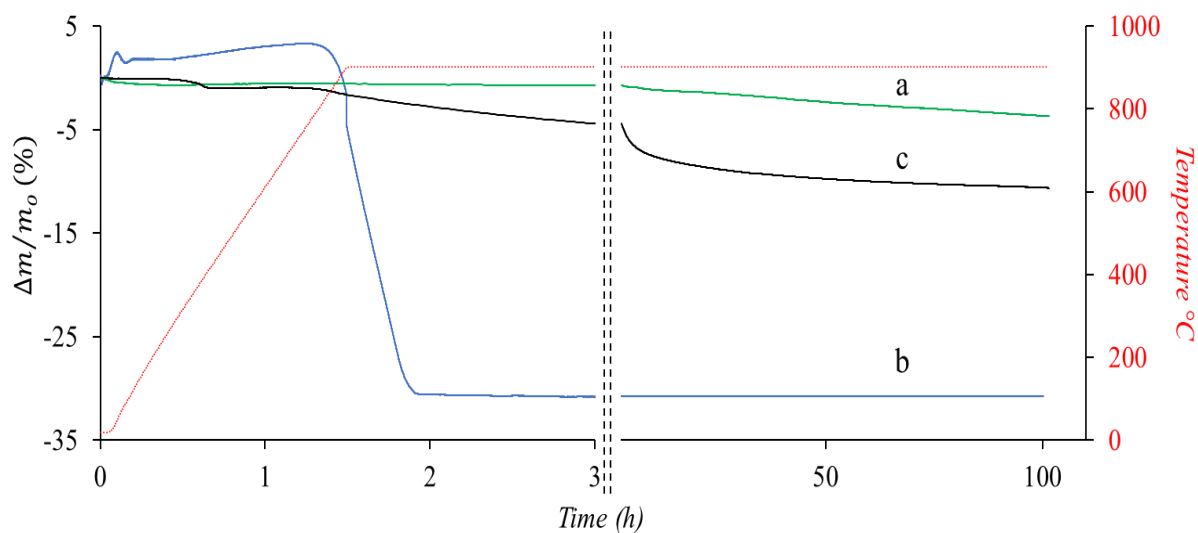


Fig.1: Mass change vs time of a) Na_2SO_4 , b) Ag_2SO_4 and of c) the 10 mol.% $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$ mixture in air at 900°C (heating rate of $20 \text{ K}\cdot\text{min}^{-1}$ and gas flow rate of $20 \text{ ml}\cdot\text{min}^{-1}$)



Fig.2: Broken $\text{Ag}/\text{Ag}_2\text{SO}_4$ reference electrode after 195 h immersion in Na_2SO_4 at 900°C . The photo displays the Ag sponge formed in place of the initially 1 mm in diameter Ag wire.

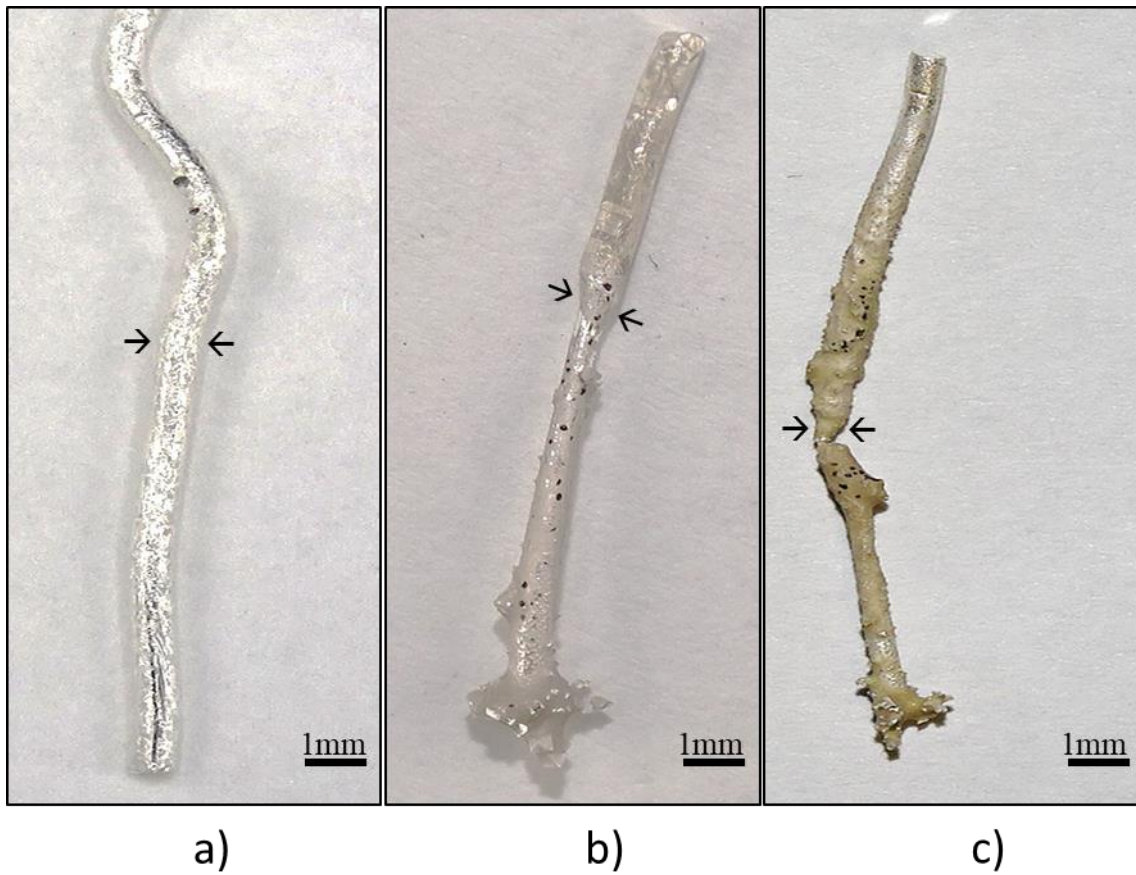


Fig.3: Macroscopic views of Ag wires partly immersed in a) Na_2SO_4 , b) 10 mol. % $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$ and c) 10 – 56 – 44 mol. % $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{MgSO}_4$ molten salts for 96 h at 900°C in air. The black arrows indicate the limit between the immersed and outer parts of the Ag wire

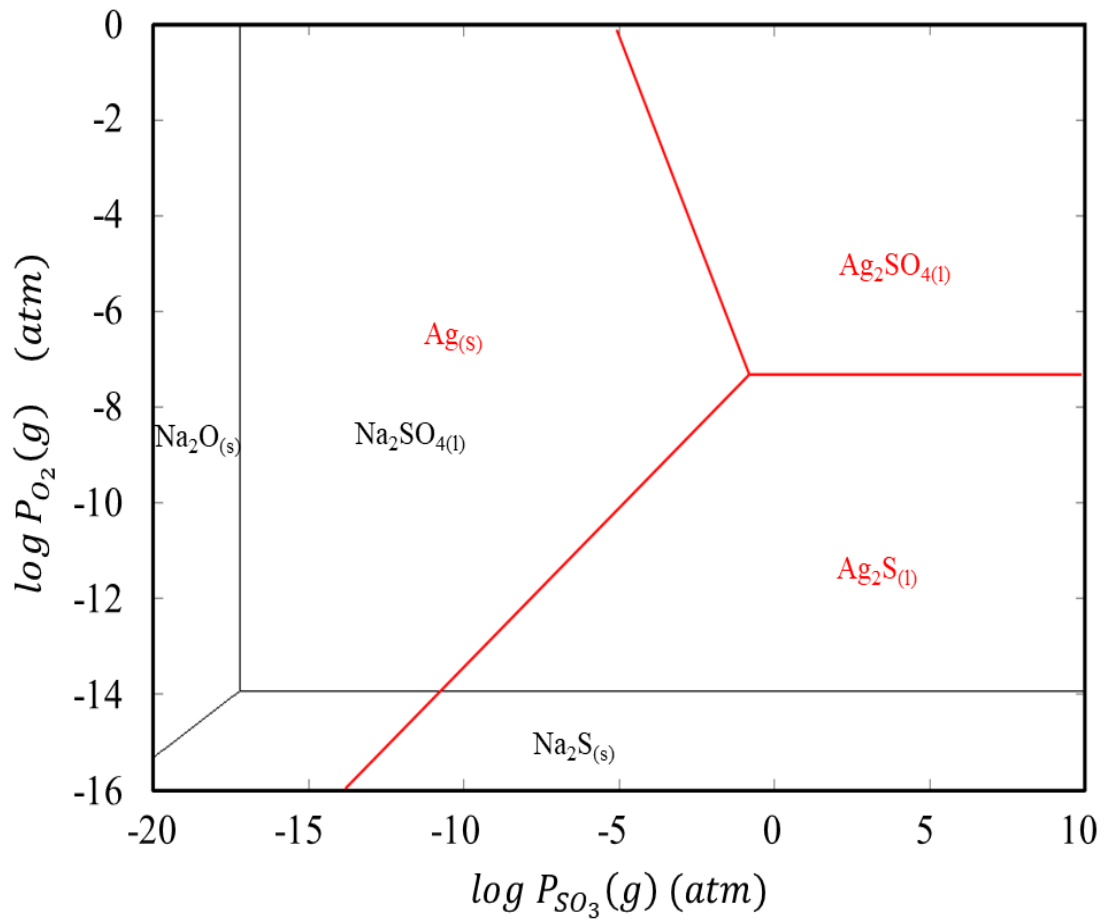


Fig.4: Kellogg diagram of the Na and Ag systems in presence of sulfate ions, drawn at 900°C with activity of the ionic species Na^+ and Ag^+ equal to 1 and 0.1 resp. [15-16]

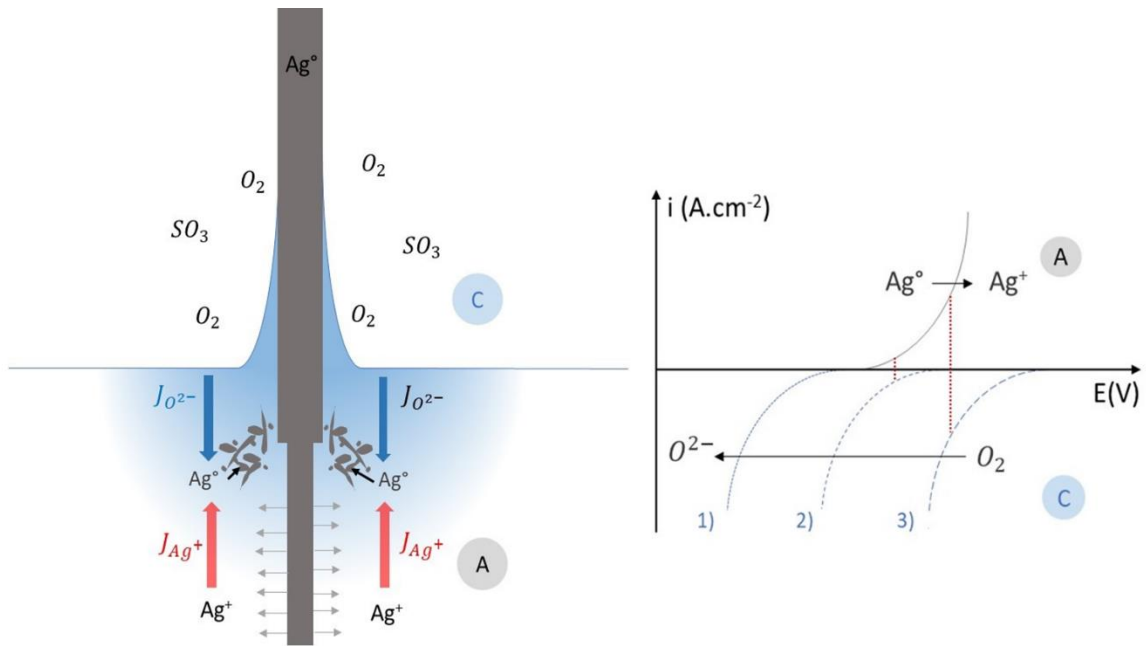


Fig.5: Sketches of a) the differential aeration corrosion settling between the anodic (A) immersed and cathodic (C) emerged parts of the Ag wire; b) the current-potential curves for the involves systems according to the acidity of the melt 1) Na_2SO_4 , 2) 10 mol. % $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$ and 3) 10 - 56 - 44 mol. % $\text{Ag}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{MgSO}_4$.