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Effect of oxygen concentration in liquid tin fuel cell's anode on corrosion behaviour of Inconel600, SS316 and Titanium

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Abstract

Effects of oxygen concentration in the liquid tin anode on the corrosion behaviour of Inconel600, SS316, and Titanium grade 2 were investigated. Owning to the high solubility of oxygen in liquid Sn, various amounts of oxygen can be dissolved at different temperatures leading to the formation of corresponding compounds on the metallic surfaces. The compounds formed are able to be leached out in dynamic system causing the corrosion such as pitting. The results showed that SS316 demonstrated highest resistance to low oxygen-containing liquid Sn. The formed Ni_3Sn_4, Fe_3Sn_2, and Sn_xTi_y are the main cause of the corrosion of the materials.

Keywords: *Liquid tin, oxygen solubility, inconel600, stainless steel316, titanium*

1. Introduction

1.1 Liquid metal reactors

The liquid-metal-fuel reactor concept has been widely developed for advanced nuclear energy for electricity production for more than 15 years. Liquid metals were first considered as reactor coolants, and later as fuel carriers. The basic simplified concept of a ship-based nuclear reactor is to use liquid metals, such as lead-bismuth, in a looping-type reactor using a relatively large pipe for circulating the liquid metals. It is actually similar to the concept of liquid-metal anode fuel cell reactor that utilizes circulations of a liquid metal for power generation but the liquid metal in a fuel cell reactor is alternatively used as an oxygen carrier. The liquid-metal-fuel-reactor concept was first suggested by von Halban and Kowarski in 1941 [1] but not further developed until 1947 when a thermal, power-generating reactor employing a solution of uranium in bismuth was chosen due to its low melting point and low neutron capture cross section of bismuth, which is undesirable for a nuclear reactor. Due to low-melting point but high-boiling point of bismuth, the high-temperature operation of a bismuth-cooled nuclear reactor has a benefit of relatively low pressure operation lowering the risk of damage from explosion. This type of reactor was desirable due to the need of a nuclear reactor system to achieve comparable efficiencies (~40% efficiency). The liquid metal in a nuclear reactor, such as bismuth, can help reduce the reactor outlet temperature in the neighbourhood of 500 °C, which is one of the pros of a liquid metal system [1].

In addition to nuclear reactors, the liquid metal is taken into consideration for solid oxide fuel cells (SOFCs) due to several benefits such as reduced direct contact between fuel impurities such as sulphur and solid anode which can poison the anode (usually Ni). Although SOFCs can operate with a wide variety of fuel sources, at high operating temperatures of conventional SOFCs (ca. 750-1000 °C), trace elements/contaminants contained in these fuels increase the electric ohmic resistances of their materials, reduce the electrochemical reaction rates, and cause material phase changes resulting in mechanical failure by reacting with the anode materials. To cope with the impacts of such reactions, increasing the robustness of the anode materials to improve tolerance for exposure to contaminant materials is needed.

Tin is an ideal anode material for such SOFCs as it is available, low cost in auxiliary power unit (APU), non-toxic, not poisoned by sulphur, carbon (fuel), and also has other wide industrial applications [2-3]. Also, liquid tin is a unique anode for direct coal input as a result of being in liquid phase (no physical structure), high contact with fuel, and allowance of the gravimetric separation of ash [4].

Liquid tin anode-carbon air fuel cell (LTA-CAFC) is an unconventional high temperature SOFC using carbon-based fuels. LTA- CAFC still uses conventional SOFC electrolyte (YSZ) and cathodes but applies an anode based on liquid tin instead of a solid anode [5]. The LTA- CAFC is a metal-air fuel cell with continuous regeneration of the metal oxide produced [2]. The liquid tin anode is the key feature of the LTA- CAFC because it can run on any carbon-containing fuels including solid, liquid, and gas without reforming or other fuel processing and also offers a higher degree of tolerance to coal contaminants that poison conventional nickel-based anodes [4-6].

A number of other advantages of a liquid metal system over aqueous or solid systems are given as follow:

(1) Liquid metals contain better heat-transfer properties than water
(2) Metal can be operated at high temperature without causing high pressures
(3) Metal systems can be used for thermal reactors because the critical mass requirement are not excessive
(4) Liquid metal can be circulated by electromagnetic pumps if required, even though the efficiency is probably low
(5) Some suitable metals are not expensive

Liquid-metal systems somehow have disadvantages over aqueous systems as listed below [1, 7]:

(1) Liquid metals are more difficult to pump
(2) Liquid metals have higher density, which may be a disadvantage when the system needs to operate on a low density fuels
(3) The high melting point of most metals makes the start-up of a reactor difficult
(4) One of the key limitation of design and application of liquid metal/alloy coolant systems in the ability of available structural materials to resist corrosion

The corrosion by liquid metals/alloys can change the microstructure, composition, and surface morphology of the structural materials affecting the mechanical and physical properties of reactors. Therefore, high temperature physical and chemical interactions with liquid metals of structural materials can cause a system failure for liquid metal systems that is extremely undesirable, in high-temperature fuel cells in particular.

Accordingly, the main objective of this work is to investigate the possibility of several metallic/non-metallic materials to be used in the liquid tin system as structural components, in which O_2 is transferred and dissolved at different concentrations for power generation, at high temperatures.

2 Material and methods

2.1 Chemicals and instruments

2.1.1 Tin

Reagent-grade granulated tin used in this study was provided by Riedel-de Haën, Germany and was of 99.85 wt% purity with the following impurities: Antimony 0.05 wt%, Bismuth 0.02 wt%, Copper 0.01 wt%, Iron 0.02 wt%, and Lead 0.05 wt%.

2.1.2 Oxygen sensors

Modified 2-wires oxygen sensors (used as a solid electrolyte) used in this study to measure open-circuit voltage, current density, and power densities of the cell were obtained from Shepshed Auto Spares Ltd. in the form of a cone (after removal the metal cover and the thread of the sensor) with the slant height of 25 mm and the cone radius of 3.5 mm. The sensors made up of ZrO_2-Y_2O_3 coated with Pt wires were used as lead wires for the melt to measure electromotive forces (emf's). The emf's shown values of the cell were obtained via U1252A handheld digital multimeters from Agilent Technologies. The pictures of the real sensor and a drawing of the oxygen sensor for surface area calculation are shown in Fig. 1 (a) and (b), respectively.

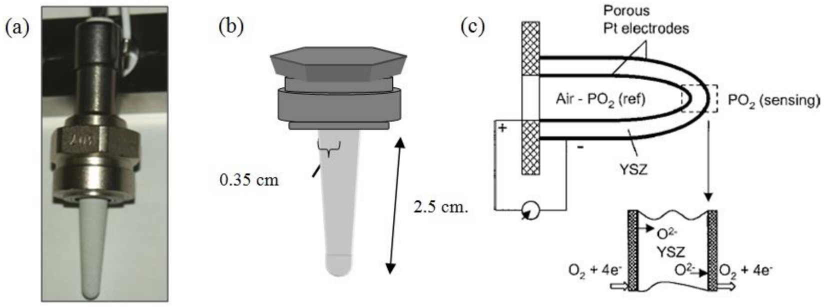

Figure 1 (a) Two wires oxygen sensor used in this study (b) Oxygen sensor's dimension (c) Schematic diagram of a potentiometric oxygen sensor employing s thimble YSZ electrolyte and platinum electrodes [7]

2.1.3 Liquid tin reactors

The metallic/non-metallic reactors that are tested in this work include:

(1) Inconel 600 reactor: as it possesses a very high melting point and excellent high strength workability at high temperatures, typical of SOFCs, Inconel600 was chosen as a material of construction for a prototype design of a batch electrochemical reactor. The Inconel600 (a nonmagnetic, nickel-based high temperature alloy) reactor was cylindrical in shape in the form of 60 mm outer diameter (O/D), 25 mm inner diameter (I/D) and 69 mm in length, providing approximately 16 cm^3 in volume.

(2) Stainless steel 316 (SS316) reactor: two stainless steel grade 316 (Fe >50 wt%, Cr 16-18.5 wt%, Ni 10-14 wt%) reactors were built in a manner similar to that of the Inconel600 reactor having a cylindrical shape. In addition, by mounting a fitting underneath the reactor this would facilitate transfer of used-liquid tin after operation without physically disturbing any protective oxide/compound layer at the reactor-liquid tin interface.

(3) Titanium (Ti) reactor: Another attempt was made by selecting titanium to replace and use as the reactor body for the small batch electrochemical reactor with similar design but without using fittings underneath to feed the bubbling gas (which were tended to be blocked by solid tin). Ti was selected because of it naturally resist tin corrosion due to its theoretical stable oxide phase. The fittings were removed from Ti O_2-sensor design because of the self-welded of the stainless steel fittings. Applying Ti for construction of the electrochemical reactor resulted in dramatic weigh reduction. Ti material would help increase the temperature threshold due to its very high melting point.

(4) High-density alumina reactor: a ceramic liquid tin bath with cylindrical shape, one open-end with small radius on edge, and flat bottom. A high purity alumina (Al_2O_3 content >99 wt%) ceramic with 30 cm height, 80 mm O/D, 66 mm I/D, purchased from Almath Crucibles LTD., UK has been chosen as the liquid tin container to avoid corrosion with liquid tin. The crucibles were made of

re-crystallised alumina as it has high melting point (can be used up to 1750 °C), and good thermal shock resistance.

2.2 Experimental

2.2.1 Experimental set ups

The principle setup of the oxygen sensor cells used for the actual reactor temperatures, open-circuit voltage, current density, and power density measurements, are shown in Fig. 2-3.

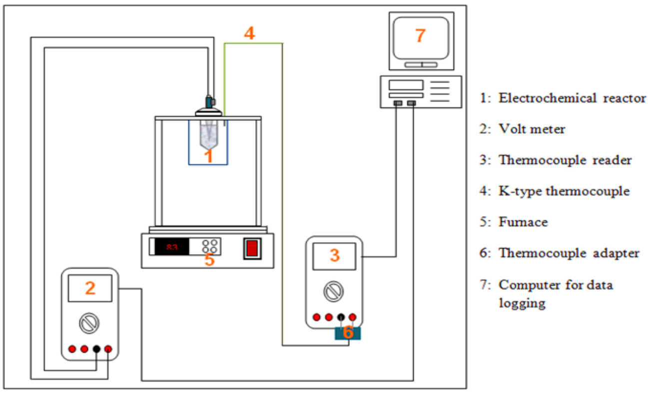

Figure 2 Schematic diagram for OCV and temperature measurements

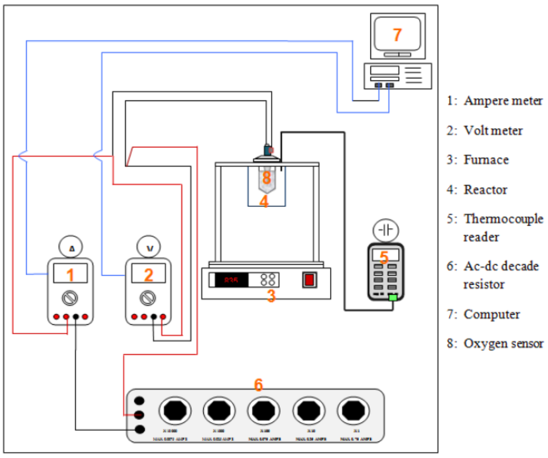

Figure 3 Schematic diagram for i-V measurements and O_2 pumping

This test rig uses a HORBACH TECHNIK furnace, K-type thermocouple, and Agilent multimeters. Radiated heat is distributed along the length of the electrochemical reactor (chamber) via the furnace to melt the loaded tin. In this manner, the chamber is gradually heated up to the desired operating temperatures, using average ramp rate of 3 °C/min. Minimum practical operating temperatures should be by around 100 °C above the melting point of the tin (232.1 °C), which is about 350 °C. Nevertheless, due to the low conductivity of the YSZ , the operating temperatures were set up higher to improve the performance of the oxygen sensor. In this study, the set of the operating temperature range is set up to 800 °C.

2.2.2 Experimental procedure

Tin was loaded into a cavity inside these reactors in quantity corresponding to 20 mm and 20 cm **(**for the alumina reactor**)** height in the liquid state of tin, respectively**.** The multi-meters displayed and recorded the electromotive force (EMF) response of the sensor as a function of time when interfaced with a computer**.**

1) OCV/temperature measurements: the electrochemical cell arrangement is also schematically represented in Fig. 2 Several runs of open circuit voltage (OCV) measurements were conducted using the same oxygen sensor each time for a set of temperatures in order to confirm the consistency of the OCV values as a function of temperature. The chamber was heated up and held at the desired temperature for around 15 min to allow the temperature to become stable. Next, the OCV's were read at each defined temperature for 30 min using a multimeter and then the OCV data were transferred to a computer.
2) Power density measurements: electrochemical cells were carried out using two multimeters to measure the voltages and the currents, and a DC decade box to regulate resistances. The obtained voltages and currents at various temperatures were collected and transferred into a computer. The schematic diagram for power density measurements is shown in Fig. 3.
3) Oxygen transfer: a constant resistance was set at the resistance box and then connected to the cell at both electrodes. The data were monitored and recorded through the Agilent multi-meters with USB connectors to a computer. Each experiment was conducted for longer than 12 hours at 800 °C.

One of the problems associated with liquid tin anode fuel cells is the formation of tin oxide (SnO_x) at the electrolyte surface when operating under load conditions. The oxide film would reduce the overall performance of the cell. Since the fuel cell performance is assumed to be bound by the limiting charge transfer at the YSZ surface, the effect of induced turbulence using inert gas purging (dry He) in the anode compartment may be a possible solution to minimise the growth of oxide films.

3. Results and Discussion

3.1 Batch scale O_2 reactors

Significant degradation of the Inconel reactor occurred after prolonged operations of the electrochemical cells. The internal walls of the cell showed up to 1 mm deep pitting, which was entirely unexpected. This result suggests that alternative reactor materials need to be found which can survive the high temperature conditions required for the cell to operate in a reducing environment. The high-temperature ceramic materials generally employed as molten metal containers such as dense Alumina are considered hence being used for scaled-up reactor.

The constructed reactor was generally very durable and easily machinable. Unfortunately, after a few long experiments (approximately 4 runs, 6-18 hours/run), severe corrosion of the reactor internal chamber was observed. Due to its high Ni content, Inconel600 alloy contains more than 70 wt% Ni, Ni is considered the main cause of the corrosion of the reactor. This can be explained by the Sn-Ni phase diagram (Fig. 4.), at the working temperature ranging from 700-800 °C, and tin concentrations higher than 50-60 mol%, liquid tin is able to dissolve a significant amount of Ni and form a more stable phase of Ni_3Sn_4. When used tin was removed from the reactor by scraping, the Ni_3Sn_4 compound was also removed from the reactor surface, causing more severe corrosion locally, so-called erosion-corrosion. As the chromium protective oxide layer (Cr_2O_3) is also removed through this mechanical treatment enhanced corrosion occurs.

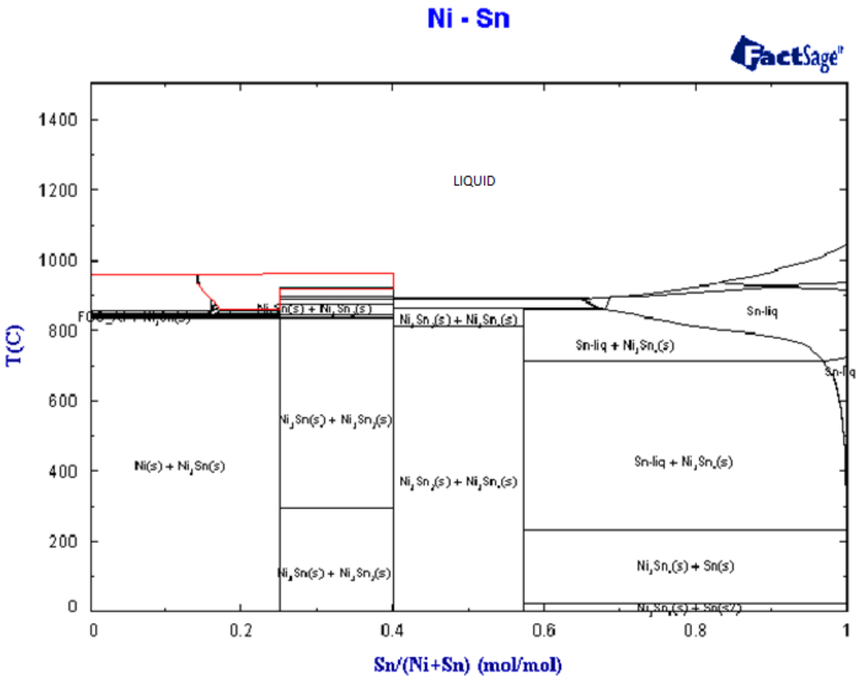

Figure 4 Sn-Ni Phase diagram from FactSage6.3

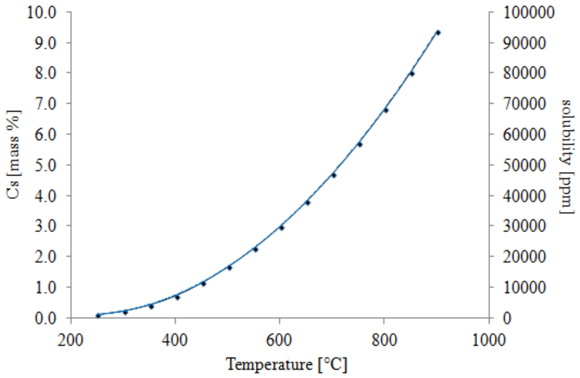

Figure 5 Nickel (Ni) solubility in tin (Sn) plotted from data in [8]

Moreover, as the temperature increases the solubility of Ni in, for example, Sn-based soldering alloys (Sn 87.5 wt-%) increases as shown in Fig. 5 [8] thereby enhancing the corrosion rate of the reactor body at higher temperatures. Fig. 5 exhibits the exponential relationship between temperature and Ni solubility.

The corrosion-prevention procedure could thus be the removal of used-liquid tin through suction in order to avoid physical contact with the internal chamber of the reactor. But suction of liquid metal is a time- and material- consuming method. Therefore, using theoretical pathways would be more logical and reliable. Several methods have been suggested in the literature to prevent corrosion of high-Ni content superalloys in liquid metals such as in liquid-lead-bismuth eutectic [9], high-Sn content soldering alloys [8]; for example: (1) Control of oxygen concentration in the liquid metals leads to the formation of a stable oxide layer on the material surface (2) Modifying the surface of the material or the material composition. In addition, alloys that contain Cr can be locally protected by diffusion of Cr to the surface and forming a chromium oxide layer, Cr_2O_3 [10]. Hence one of the alternative materials to Inconel600 is stainless steel SS 316. This is because stainless steel contains a significantly lower content of Ni, but a similar amount of Cr.

3.2 Stainless steel 316 (SS316) O_2-sensor electrochemical reactor

As expected from the chemical composition of SS316 a protective Cr-oxide layer should form at the reactor wall and corrosion would not be expected due to considerable lower amount of Ni-content in SS316. The reactor length was reduced by 1/3 in order to cut the heating time, to simplify control of temperature, and to save on cost of material as the reactor cavity (liquid tin compartment) suits the dimension of the oxygen sensors used.

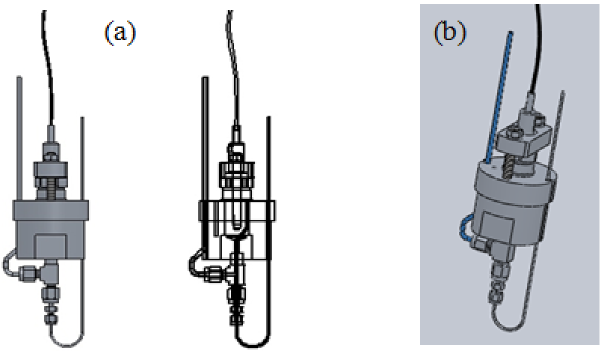

Figure 6 (a) Side view of the SS316 O_2 sensor electrochemical reactor compared to the transparent view of the same model. (b): 3D of the SS316 reactor

The dimensions of the reactor body shown in drawing-worksheet from SolidWork at front view, side view, and bottom view are exhibited in Fig. 7. Fig. 8 presents the photographs the used SS316 reactors: side-view, top-view, and bottom-view.

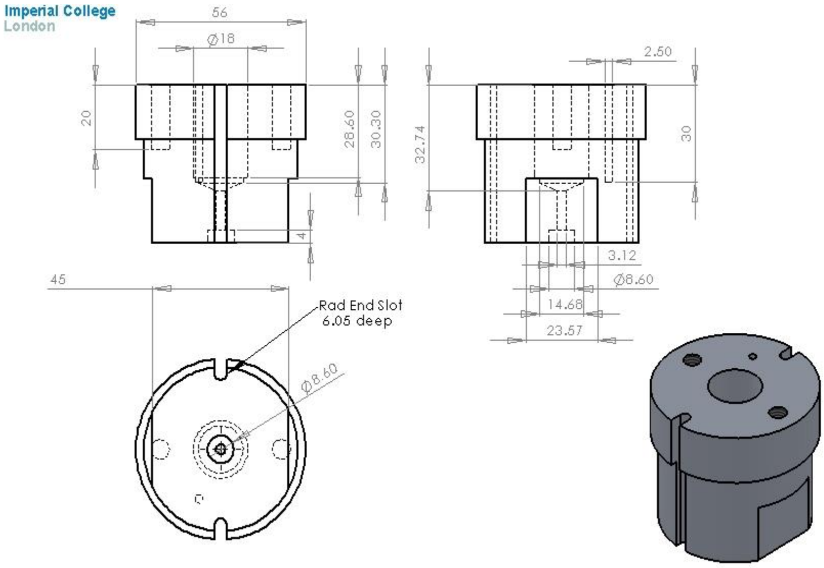

Figure 7 Schematic drawing of the SS316 reactor

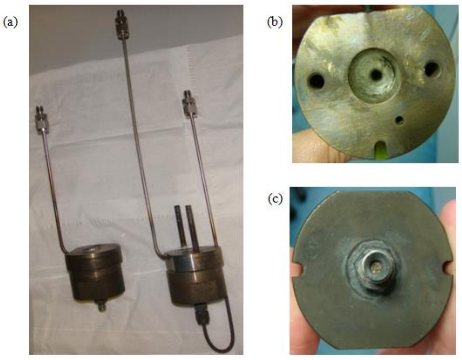

Figure 8 Photographs of the used SS316 reactors: (a) side-view, (b) top-view, and (c) bottom-view

Tin does tend to dissolve a small percentage of Fe (from the SS reactors) to form FeSn at lower temperatures after the layer of protective chromium oxide layer is reduced or perturbed. This can be explained by Sn-Fe phase diagram in Fig. 9 that Sn can hold only <0.05-2 wt-% Fe at 513-806 °C. This relatively low Fe solubility in Sn is actually a good indicator that Fe would not be easily dissolved by molten Sn at LTA-ICFC operating temperatures. To evaluate whether Fe was dissolving in the liquid Sn, tin slugs obtained from the SS316 reactor were analysed using energy-dispersive X-ray spectrometry (EDX) (see Fig. 10 (a-b)). The EDX clearly shows the presence of Cr, Fe, and Ni in addition to Sn, indicating dissolution of the SS316 body.

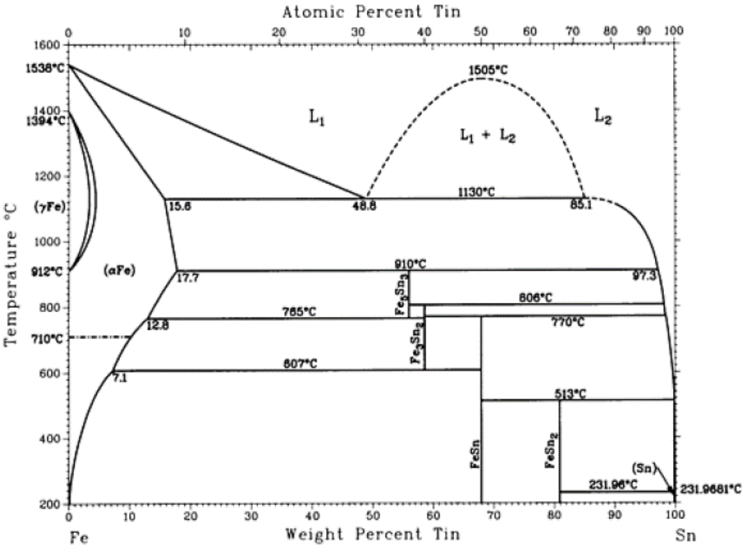

Figure 9 Sn-Fe phase diagram [10]

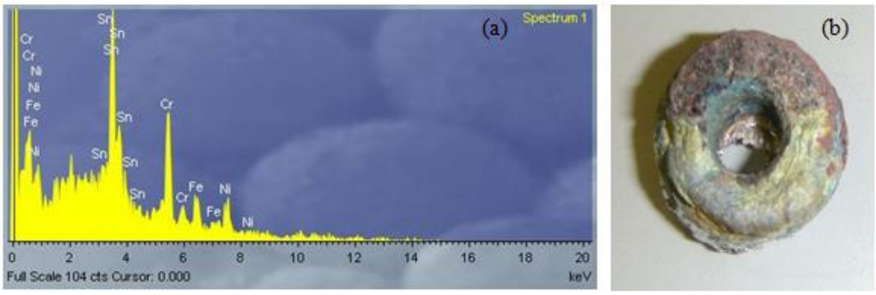

Figure 10 EDX spectrum of the tin slug (b) tin slug from SS316 reactor

As a result, it can be concluded that stainless steel reactors are also susceptible to damage, albeit at a much reduced rate in comparison to the Inconel 600 reactors.

3.3 Titanium (Ti) O_2-sensor electrochemical reactor

Another attempt was made by selecting titanium to replace and use as the reactor body for the small batch electrochemical reactor with similar design but without using fittings underneath to feed the bubbling gas (which were tended to be blocked by solid tin). Ti was selected because of it naturally resist tin corrosion due to its theoretical stable oxide phase. The fittings were removed from Ti O_2-sensor design because of the self-welded of the stainless steel fittings. Applying Ti for construction of the electrochemical reactor resulted in dramatic weigh reduction. Ti material would help increase the temperature threshold due to its very high melting point. But it is relatively difficult to bend or re-shape a Ti tube so SS316 tubings were applied as a substitute for Ti tubing.

Sn-O-Ti phase diagrams with a wide range of oxygen concentration from 10^{-20} to 10^{-5} atm were constructed and are shown in Fig. 11 (a-c), respectively. As can be seen from the phase diagrams of Sn-O-Ti the oxide of Ti is formed at all oxygen concentration in the range being considered. This implies that if there is a sufficient amount of oxygen dissolved in the liquid tin, TiO_2 would form at the Sn/Ti interface and would be expected to prevent the corrosion of the Ti reactor body in the working temperature range from 700-800 °C without using high turbulence of bubbling gases.

Since titanium seems promising as a constructional reactor/component for liquid tin, some Ti tubes were used for the large ceramic reactor as gas feeding lines and current collectors. The Ti tubes were tested with liquid tin at 700-800 °C with and without He gas. Unfortunately, it was found that the Ti tubes were severely corroded by molten tin, and more severely when the He gas was used. Therefore, the usage of Ti O_2-sensor reactor was suspended to prevent the damage of the reactor and the whole system. Under the circumstances, the attention for liquid tin container and components was alternatively paid to ceramic materials and graphite. The completed Ti O_2-sensor reactor, assembled reactor (from Factsage6.3), and its components are presented in Figs. 12 and 13.

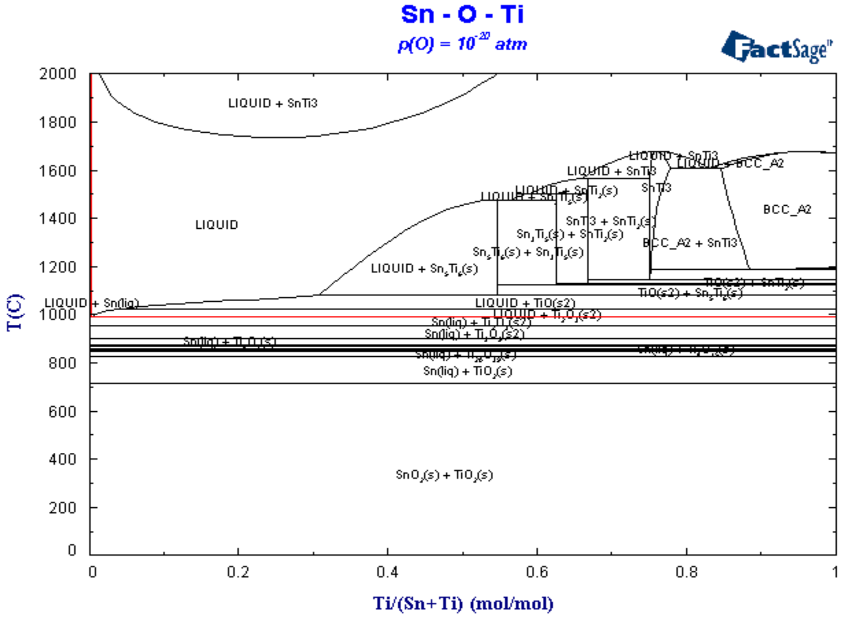

Figure 11 (a) Sn-O-Ti tertiary phase diagram with oxygen concentration (pO_2) at 10^{-20} atm

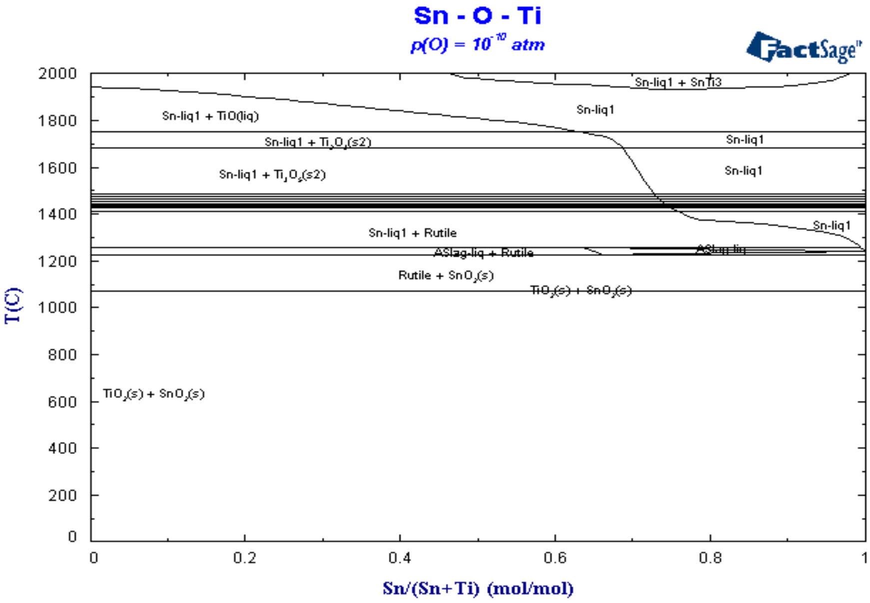

Figure 11 (b) Sn-O-Ti tertiary phase diagram with pO_2 at 10^{-10} atm

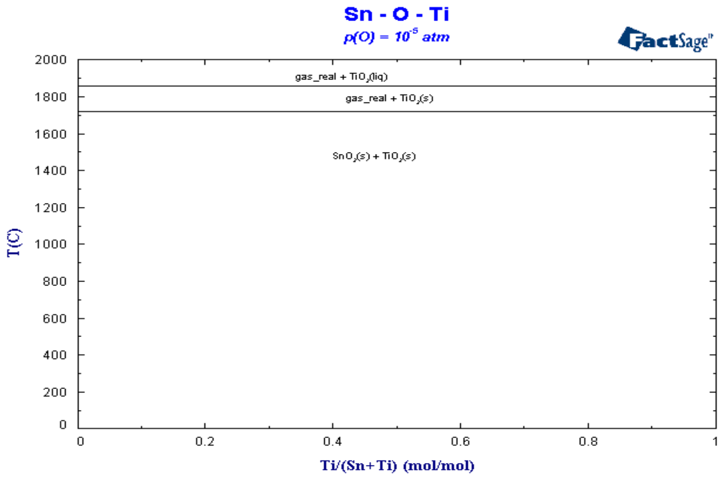

Figure 11 (c) Sn-O-Ti tertiary phase diagram with pO_2 at 10^{-5} atm

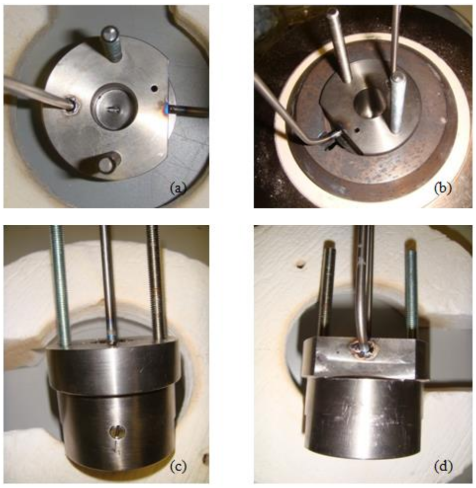

Figure 12 Ti reactor short version with a side-plug

Ti tubes have advantages over ceramic tubes in terms of thermal expansion coefficient, better thermal-cycling tolerance, and higher strength. With respect to accommodating of the cell's arrangement Ti tubes can be easier constructed than ceramic tube. However, after a few electrochemical measurements were conducted corrosion of all Ti tubes was observed. All gas inlet lines were thus changed to alumina tubes to prevent corrosion and also help reduce cost. Fig. 13 shows all the corroded Ti tubes immersed in liquid tin with the colour of the TiO_x on the surface [11].

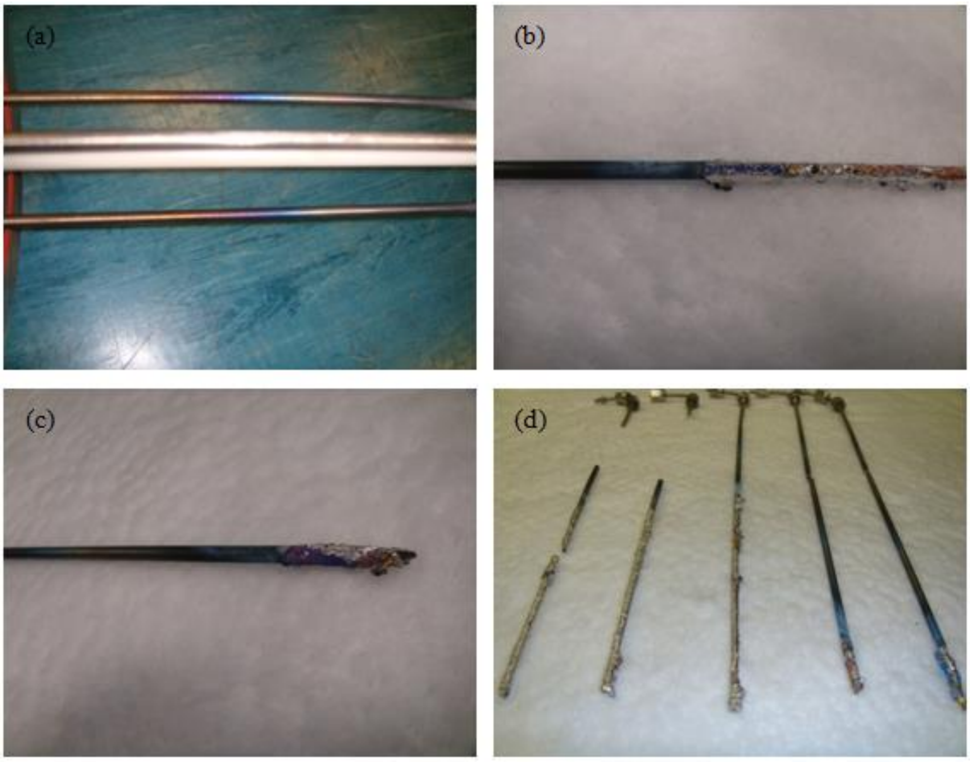

Figure 13 Ti corroded tubes used at various immersion times

The phase diagrams of Ti-O-Sn in Figs. 11(a-c) and Ti-Sn in Fig. 14 were used to explain this phenomenon. Despite the fact that when the Sn-Ti system contains a certain amount of oxygen $TiO_{x(s)}$ will form to prevent the corrosion of the tubes (e.g. $pO_2 = 10^{-20}$, Fig. 11 (a)), the low oxygen concentration in the molten tin leads to the dissolution of Ti into the liquid tin. The formation of intermetallic compounds at the Ti-Sn interface is expressed by Eq. (1):

$$\mathrm{xSn}_{(l)} + \mathrm{yTi}_{(s)} \leftrightarrow \mathrm{Sn_xTi_y}_{(s)} \tag{1}$$

where x and y can be 1, 3, 5 and 2, 3, 5, 6 respectively [12]. Since the amount of liquid tin contained in the reactor was considerably higher than that used in the batch-scale electrochemical reactor, the oxygen concentration to form a titanium-oxide layer was not reached. It is therefore concluded that at working temperatures of 700-800 °C, from >0.40 mole fraction of Sn (see Ti-Sn phase diagram in Fig. 14) some intermetallic compounds such as $Sn_3Ti_{5(s)}$, $Sn_5Ti_{6(s)}$, and $Sn_3Ti_{2(s)}$ mixed with liquid tin are formed. Since the oxygen concentration was below the equilibrium concentration for the formation of protective layers, the Ti tubes were found suffered by the observed dissolution.

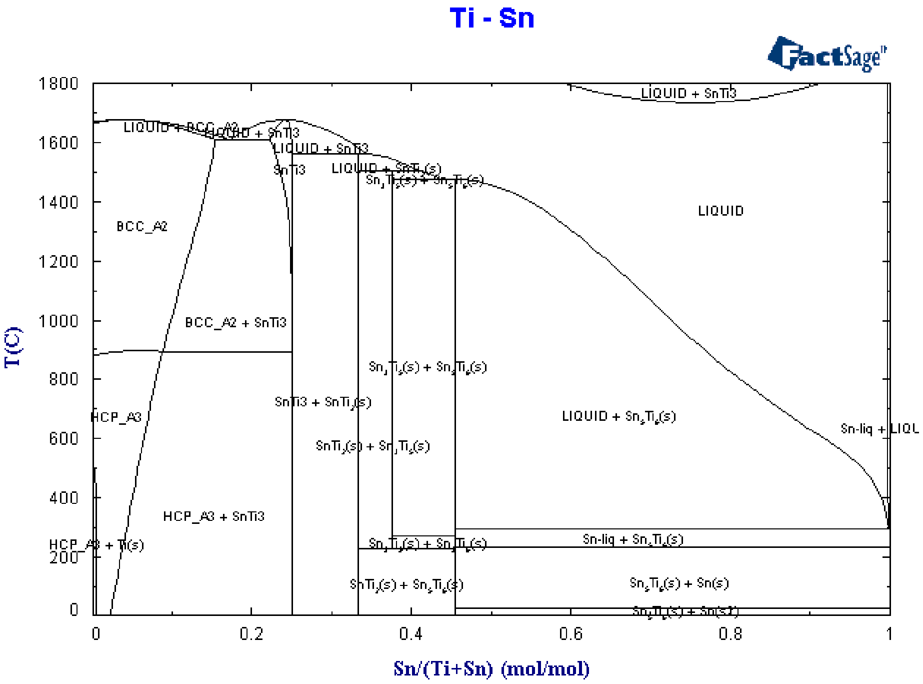

Figure 14 Ti-Sn phase diagram

4. Conclusion

Employing liquid metal anode for a fuel cell provides a number of advantages over other types of fuel cells. A number of benefits from applying liquid tin anode are given as follow;

- Low vapour pressure (p):
- $\log p = -9.32188 - \frac{14023.92}{(T)} - 8.8122E^{-4}(T) + 5.6201(\log T)$,
  where the applicable temperature (T) is 1424<T<1753 °K. [13]
- Low melting point (231.9 °C) [13]
- Relatively high oxygen solubility
- Slower oxidation rate than other liquid metal such as lead, bismuth, or lead-bismuth eutectic (LBE)
- Not poisoned by sulphur, carbon
- Comparatively low cost
- Non-toxic to environment/operator unlike Hg, Pb, Bi etc.
- Widely available due to its numerous industrial applications

The novel generation of LTA-ICFC reactors must be economically competitive, reliably safe, theoretically durable to molten tin at high temperatures, and probably light weight (for small scale applications).

Material corrosion is one of the main issues studies a lot recently in the development of the liquid metal technology. One of the key limitations of design and application of liquid metal in fuel cells is the ability of available structural materials to resist corrosion. Ceramic has a very good corrosion resistance to liquid metals, it is however, difficult to machine because of the limitation of low cost cutting tools, and very costly. The limitation of shaping/modifying of the ceramic materials results in restricted options of reactor's configuration. Hence more attention to use metals as the liquid containers has been paid. After several experiments with liquid tin of some metal constructional materials were conducted, for small batch reactors, constructional materials' oxidation/corrosion was observed. For the Ti used as gas inlets was found dissolved in the liquid tin because of no protective oxide layer formed. The thermodynamics data such as phase diagrams have been used to explain these phenomena including the information of protective oxide layer, and to discuss how to tackle the problems.

Difficulties of the reactor's design and construction, and operating problems of the liquid tin containing reactors are given below:

In particular, for those two metal alloys (Inconel600 and SS316) , and a homogeneous Ti material, in order to be able to improve the possibility for being LTA container, the selection strategy for each material is given as:

- Inconel: Inconel600 is a nickel-based superalloy. Advantages of Inconel600 include very high melting point, good corrosion resistance for static system, high strength, and easily machinable. Disadvantages are that it is impractical for turbulence system due to the damage of the protective oxide layer, and reasonably high cost.
- SS316: The formation of chrome and/or iron-chrome oxides observed from the EDX results of the tin slug obtained from SS316 reactor shows the tendency of the protective oxide layer to protect the reactor from attack. However, running experiment at high temperatures longer than 12 hours resulted in the leaching of the protective oxide layer from the reactor's wall. Although the CrO_x film was damaged from the reactor surface, the reactor did not seem to extensively suffer from the dissolution of the main composition of SS316, which is Fe. This is because the solubility of Fe in Sn is very low [14]. In the case of SS316 reactor, it can be concluded that the protective oxide film was destroyed from the induced turbulence of the system from feeding gas. Therefore, it might be possible to use SS316 material as a liquid tin container with a stagnant operation.
- Ti: Even titanium is naturally resist tin corrosion because of its stable TiO_2, the magnitude of system's turbulence and actual oxygen concentration in the molten tin must be considered. As temperature increases, the amount of Ti that can be dissolved into Sn increases at faster rate than does Fe (in SS316) (see phase diagrams). Consequently, application of titanium at high temperature in the system containing reasonably very low oxygen concentration is not recommended. Moreover, even the oxygen concentration in molten reaches the value that TiO_2 could form, the system with induced turbulence is also unprofitable.

In addition, corrosion, erosion, safety problems are much more severe with liquid-metal system, especially LTA-ICFC, because it operates at high temperatures and long exposure time. The apparent severity of damages are of the following order Ti > SS316 > Inconel 600 (locally corroded). The main form of Inconel 600 is the local erosion while of the SS316 and Ti are leaching of Cr-O protective film due to gas turbulence and the dissolution of material owing to the limitation of pO_2 in the molten tin, respectively. There are two possible patterns relating to the corrosion/dissolution of the material in liquid tin.

Firstly, for oxygen concentrations below the equilibrium concentration for the formation of protective layers, metal container/components will suffer corrosion.

Secondly, at a certain level of oxygen concentration of dissolved oxygen corrosion process is suspended or taken slower due to protective oxide film formed on the surface of the metal components. For example; for Cr to form Cr_2O_3, mole fraction of oxygen has to be at least 0.6: for Fe to form Fe_3O_4 and Fe_2O_3 mole fraction of oxygen has to be at least 0.5 and 0.58, respectively in the solution, for Ti mol-% O has to be >30% to form Ti_3O_2, >40% to form TiO, > 60% to form Ti_3O_5, and >70% to form TiO_2, all data acquired in the range of 700-800 °C from FactSage6.3 and [15].

The Ellingham diagram plots (Fig. 15) the standard Gibb's free energy of chemical reactions when oxides of elements are formed as a function of temperature. By using the diagram, standard free energies of formation of oxides can be found at 0-2200 °C. Also, the equilibrium composition of the system, the oxygen partial pressure, which is particularly important for LTA-ICFC system, can be obtained through reading the diagram.

The equilibrium concentrations of oxygen for the formation of protective layers of the metal container and/or components that were employed (700-800 °C) are:

a) pO_2 of 10^{-18}-10^{-15} atm for NiO formation,
b) pO_2 of 10^{-21}-10^{-18} atm for SnO_2 formation,
c) pO_2 of 10^{-22}-10^{-19} atm for Fe_3O_4 formation,
d) pO_2 of 10^{-32}-10^{-28} atm for Cr_2O_3 formation, and
e) pO_2 of 10^{-37}-10^{-34} atm for TiO_2 formation
f) And the degree of stability of various oxides formed in the LTA-ICFC system in the metal reactors can be relatively compared by the Ellingham diagram as $TiO_2 > Cr_2O3 > Fe_3O_4 > SnO_2 > NiO$. Accordingly the protective oxide layers of different materials suppose to form before the oxidation of liquid tin except Ni.
g) Utilising the phase diagrams of Sn-O-Ti (Figs. 11 (a-c)) and the Ellingham diagram [17], it can be seen that there should be the formation of $TiO_{2(s)}$ at LTA-ICFC operating temperatures that could protect the Ti tubes from being perturbed by molten tin. And the appearance of $TiO_{2(s)}$ film at the corroded Ti tube walls showed that the pO_2 in the liquid tin reactor was at least $\sim 10^{-37}$ atm. However the Ti tubes dissolved into the liquid tin because the interface between Ti tubes and liquid tin covering the Ti tubes is Sn-rich region containing the compositions of Sn/(Ti+Sn) higher than 0.4 mol/mol (see Fig. 14) and the pO_2 was assumed to be $<10^{-37}$ atm.
h) Since controlling of oxygen concentration in the liquid tin is more difficult than the other methods to prevent corrosion of the metal immersed in the liquid tin. On one hand, keeping oxygen transferred rate lower than the solubility limit of O_2 in tin to avoid SnO_2 formation at the YSZ electrolyte interface might lead to the corrosion of metal container/components. On the other hand, too high dissolved oxygen would also cause the formation of $SnO_2(s)$ in the bulk and hence lower efficiency. To avoid such problems, coated metals can be interesting contenders in addition to high-temperature ceramics as the structural material with respect to its tensile strength, thermal expansion, machinability etc. If necessary, pure metals such as chromium, molybdenum, tungsten might be useful as they are the most resistant to liquid tin [16]. However, if the system does not require substantially fast start-up time such as for portable devices and stationary applications, ceramic materials can still be employed with lower cost of production in comparison to processed metals or especially metal alloys.

Moreover, the negative absolute value of the Gibb’s free energy of the formation of metal oxides are smaller as the temperature increases, which can be implied that the oxides are unstable and easy to reduce at higher temperatures. The metals that appear higher up on the diagram are more stable because the standard Gibb’s free energy is lower (less negative) than those metals that appear lower down (but some lines can cross the others at some temperatures). Hence, the reaction that the free energy is greater (more negative) relative to the other reactions, the composition is then further weighted toward the products (oxides) of the reaction. This leads to the most severe damage of the Ti tubes as titanium oxidation reaction (see Fig.15) has more negative values than those being compared. While He gas was used, the TiO_2 formed was therefore disintegrated by the turbulence of the gas stream.

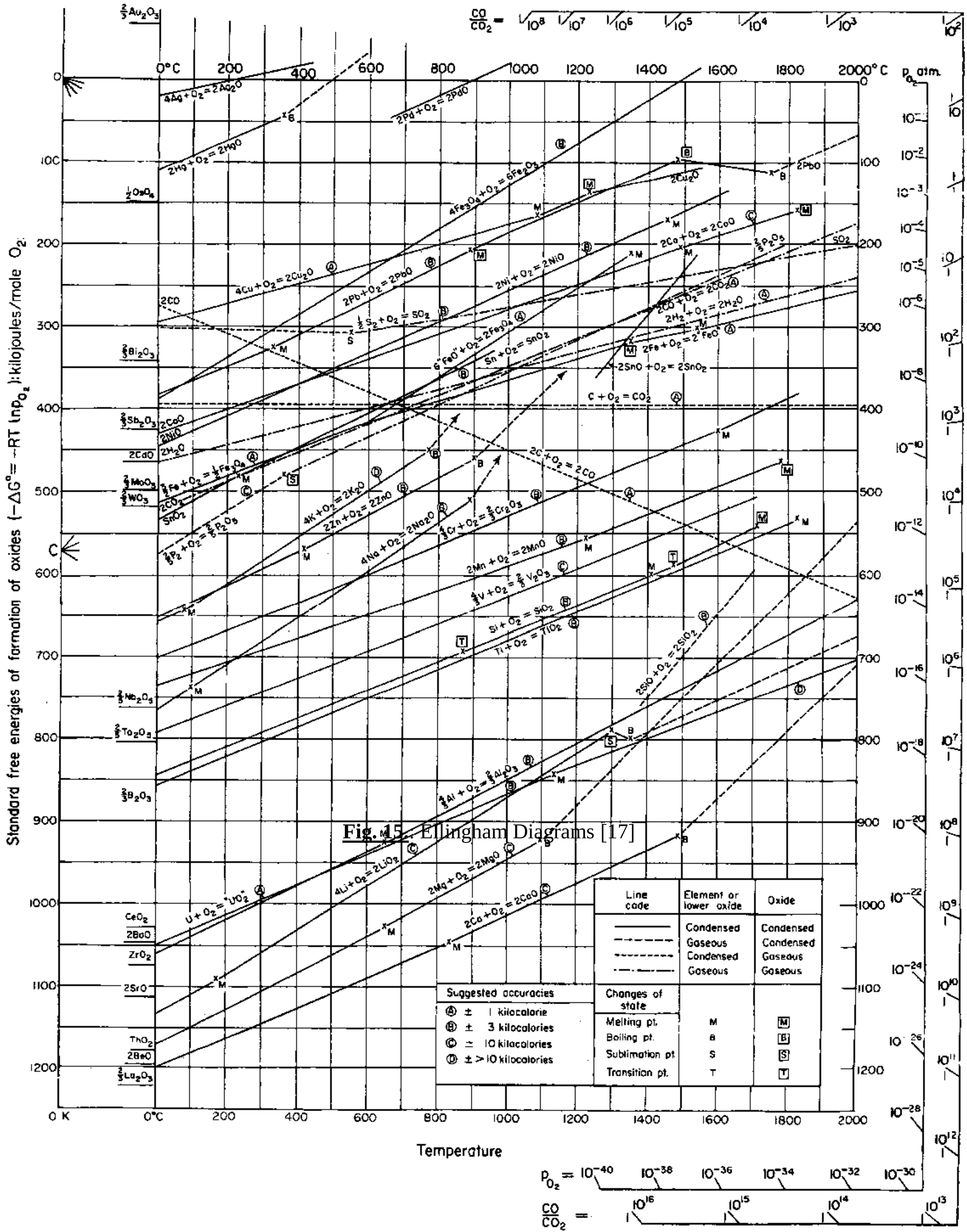

Fig. 15. Ellingham Diagrams [17]

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