Development of lining materials for reactor vessel used in the CSIR titanium process

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Abstract. The CSIR Titanium powder process is a high temperature’ molten salt /alkali metal titanium production process. The aim of this process is to produce titanium powder of high purity and quality that meets the specifications for commercially-pure powder. The quality of CSIR Ti-powder produced to date shows in general that there are challenges when it comes to meeting this requirement. Two of the main challenges is the reagents used employed in the process and by-products formed which are highly corrosive. These corrosive agents promote corrosion of the reactor with the corrosion product then being introduced as impurities in the titanium powder. A project to investigate lining materials to protect the vessel from corrosion and preserve product quality and purity was thus initiated. This article gives an in-depth insight into the corrosion resistance properties of different metals that can be investigated as a potential lining material in molten lithium and molten lithium chloride environment.

1. Introduction
South Africa is one of the leading producers of titanium mineral concentrates in the world [1]. Regardless of having these mineral reserves in abundance, the country does not have an established titanium production industry. The lack of local titanium production capacity and associated manufacturing capabilities were identified by the Department of Science and Technology (DST) and Department of Mineral Resources (DMR) as a key potential economic growth area.

In order to exploit this potential growth area, the DST initiated a Titanium center of competence (TiCOC) hosted by the CSIR. The main objective of DST through TiCOC was to develop a novel titanium powder production process that can be ultimately be commercialized. It is for this reason that the CSIR-Ti process, a novel titanium production process was developed and commissioned at pilot scale by the CSIR.

Titanium is currently being produced commercially via Kroll and Hunter processes[1,2]. These processes are both batch processes that employ metallothemic reduction of titanium tetrachloride to produce titanium. The Kroll process uses molten magnesium as a reducing agent while the Hunter process employs molten sodium. There are documented attempts where lithium and calcium were used as reducing agents as well[3]. The CSIR-Ti process differs from commercial processes as it aimed to produce titanium powder via a continuous process[1,3]. The aim of this process is to produce commercially pure titanium powder however the quality of CSIR Ti-powder produced to date shows in general that there are challenges when it comes to meeting this requirement[4].
One of the challenges of this process is that the molten metal that is used and the molten salt by-product that forms are very corrosive. These agents promote corrosion of the reactor vessel with a potential for corrosion product to be introduced as impurities in the titanium product. Figure 1 shows the severity of the corrosion caused by molten salt following a salt leak or a lack of proper sealing of the vessel. It was found that the use of a suitable reactor lining material can help eliminate or reduce contamination of the titanium metal product as well as reduce the risk of leakage caused by corrosion. The lining material should be able to resist corrosion by molten salt and/or molten metal at temperatures above 650°C, this being the nominal process temperature. A project to investigate lining materials to protect the vessel from corrosion and preserve product quality was thus initiated. In this project, different materials that can resist corrosion by molten lithium chloride (LiCl) and lithium (Li) will be identified and tested to identify the most suitable candidate.

Molten salts and molten alkali metals are mostly used in the heat treatment industry because of their good thermal properties. Even in these industries, the corrosion of the containment material is a major problem [5,6]. Despite the fact that the reagents are widely used in some industries, there is still limited information and understanding to serve as the basis for the selection of compatible materials [7]. The aim of this literature review is to highlight reported work on corrosion of different materials in molten lithium and lithium chloride environments, with emphasis on reaction mechanisms and corrosion trends. The review serves to identify the material with the most favorable corrosion resistant properties with the intention to test further under conditions representative of the CSIR-Ti process after which a lining material will be selected.

2. Molten salt corrosion

Molten salt corrosion generally occurs in two steps. The corrosion starts with oxidation, followed by the dissolution of the metal oxide of the containment metal [5]. Molten salts are good fluxing agents and can thus easily remove oxide scale from the metal surface [6,7]. At high temperatures molten salts also act as good solvents of precipitants, preventing passivation of the metal surface because oxides scales are not able to form[6,7]. At elevated temperatures molten salt corrosion is rarely inhibited because the salts become increasingly conductive and reactive, promoting electrochemical processes [6]. The presence of impurities in the salt, typically oxygen and water vapour can accelerate corrosion [7]. The corrosion resistance of metals to molten salt also depends on the elemental composition, i.e.,
Al, Si, Mo, etc. which affects the development of the passivating oxide [6]. Corrosion mechanisms in aqueous solutions may also be applied to that for molten salts. The main difference between the two systems is that in molten salts, the most active element is oxygen, therefore pO² is applied instead of pH [7]. Due to these similarities, the corrosion that applies in aqueous environments are also applicable in molten salt, be this in the form of uniform surface corrosion, intergranular corrosion, galvanic corrosion and pitting[5–7].

LiCl is produced as a by-product when Li is used as a reducing agent in the Ti-metal production process from TiCl₄. Understanding the corrosion behavior of different containment materials exposed to molten LiCl is therefore very important. Although the corrosion studies of potential containment material against molten LiCl is limited, the articles referenced below help clarify this issue and provide useful information.

Shanker et al intensively investigated high-temperature corrosion of Ni and Fe alloys in molten LiCl-KCl medium in different atmospheres[8–10]. Alloys such as 316L stainless steel, Inconel 600, Inconel 625, and Inconel 690 were investigated for corrosion in different tests with temperatures ranging from 650–850 °C for extended periods of time. The authors derived the following conclusions based on their experiments; selective leaching of Cr by molten LiCl is responsible for corrosion experienced by these alloys[8–10]. Other authors like Cho et al[11,12] and Indacochea et al [13] tried to study the corrosive properties of molten LiCl and molten LiCl-Li₂O in oxidizing and inert atmospheres.

Cho et al [11] made an observation that the corrosion rate of the Fe/ Ni alloys in molten LiCl is relatively low and the weight losses are similar but the addition of Li₂O to LiCl significantly accelerates the corrosion rate. They also noted that the corrosion rate increased with the Cr content of the alloys tested [11]. Indacochea et al [13] thus concluded that that corrosion mechanism of these materials in molten salts is different in oxidizing and inert atmospheres.

The corrosion reaction of molten salts proceeds by oxidation which is then followed by the dissolution of the metal oxide [5]. Ni and Fe alloys contain a certain percentage of Cr in their matrix, which is responsible for forming a passive Cr₂O₃ layer which acts as a protective barrier against corrosion in aqueous systems. Molten LiCl is a good fluxing agent that effectively removes and dissolves Cr₂O₃ scales from metal surfaces [5,9]. The conclusion that was made by Shanker et al [8–10] was supported by Salinas-Solano et al [14], who reported that Cr is more soluble in molten chloride salts when compared to Ni and Fe, and is therefore responsible for low resistance of some Cr-containing metals in oxidizing, molten salts environments.

The observation made by Cho et al is as a result of the introduction of oxygen ions into the system by Li₂O. It is reported that oxygen ions penetrate through the micro-channels formed in the alloys to induce internal, inter- and trans-granular corrosion[12–14]. The microchannels are formed when iron diffuses into the Cr₂O₃ layer and then dissolving in the molten salt, forming voids between the Cr₂O₃ layer and Ni-rich oxide[8]. The diffusion of Fe-ion takes place because Fe-ions have more cation defects compared to Ni ions in the Ni-rich oxides [12]. Therefore Fe also contributes to the overall corrosion of Fe and Ni alloys in molten salt environments. Shanker et al [10] reports that the better corrosion resistance properties of Ni-based alloys to molten LiCl can be attributed to the adherent and protective NiO present on the surface. Cho et al [12] made a similar observation and reported that the accumulation of Ni around the inner oxides of the alloy delays corrosion rate. In conclusion, Ni-based alloys are more resistant to molten LiCl corrosion than Fe-based alloys and the resistance to molten LiCl increases with decreasing Cr and Fe content and increasing Ni content in Fe-Ni-Cr alloys[11,10].

3. Molten metal corrosion

Molten metals are mostly used as heat transfer medium because of their excellent thermal properties such as high thermal conductivity, heat capacity and low vapour pressures [5]. Molten metals also serve as reducing agents in the production of metals[15]. Molten alkali metals like Mg, Na, and Li are used in the production of titanium with magnesium being the most common as per the Kroll process. One of the biggest challenges when working with molten metals is the corrosion of the containment
metal (solid metal) by the liquid metal. Molten metal corrosion can be defined as the interaction which takes place between a solid and metal in the molten state [16]. This type of corrosion is mostly caused by the solubility of solid metal into the liquid metal. In this section of the review, the molten metal of interest is Li. In general, molten Li corrosion mechanisms can be classified as a combination of the following interactions: dissolution (uniform), impurities and interstitial reaction (inter- and trans-granular attack), alloying and compound reduction [6,15,16].

3.1. Direct dissolution

Direct dissolution is the simplest and most dominating form of molten Li corrosion. Direct dissolution takes place when solid metal atoms are released and dissolved into the molten metal in the absence of impurities [15]. Solid metals that have high solubility in molten Li will generally exhibit a higher corrosion rate [5].

Tortorelli [15] derived a mathematical expression (Equation 1) that can be used for explaining molten Li metal corrosion by dissolution. Based on the equation, corrosion by direct dissolution can be reduced by selecting a containment metal that has low solubility in molten Li or saturating molten Li with another reagent to reduce its ability to dissolve before exposure. Saturating molten Li before the exposure is however not ideal for the titanium production process due to the risk of introducing impurities into the final product.

\[ J = K(C - c) \] (1)

J - Rate at which elemental species enter the solution,
C - Solubility of a particular metal in the molten metal,
C - Actual concentration of the metal in the molten metal,
K - Solution rate constant of the rate-controlling steps

The solubility of different metals in molten Li was investigated by Cleary et al [17] and the results are shown in Figure 2. Based on this study, Ni has the highest solubility in molten Li compared to Cr and Fe [17]. The susceptibility to dissolution attack in Ni-Fe-Cr alloys increases with an increase in nickel content[17]. Quain et al [18] studied the corrosion of austenitic stainless steels in molten Li and found that the corroded region of the metal had depleted Ni and Cr. In the affected region, Ni and Cr were reduced by 89-91% and 91-93% respectively. The authors then concluded that the corrosion process of the metal was due to the preferential dissolution of Ni and Cr into the molten Li [18]. It is for that reason that Ni and its alloys are normally not considered good candidate materials for containing molten Li [5]. The presence of nitrogen and carbon impurities in molten Li promotes the diffusion of Cr into the molten Li and would thus accelerate the corrosion [19,20]. Olson et al[19] report that based on the nature of dissolution attack of ferrous alloys, alloys with limited Ni and Cr content are more desirable [19]. The authors’ further state that pure Fe demonstrated good corrosion properties to molten Li [19]. Figure 2, also shows that refractory metals have low solubility in molten Li when compared to Fe and Ni alloys. Investigations also indicate that refractory metals can resist the dissolution corrosion mechanism when the system contains no impurities, especially oxygen [21,22]. The effects of impurities on molten Li corrosion is discussed in the next section.
3.2. Impurity or interstitial corrosion

Impurity or interstitial reactions refer to the interactions of light elements present in containment materials (interstitial) or in the molten metal (impurities) [5,6,16,21]. The impurities active in molten metals corrosion are oxygen, nitrogen, carbon, and hydrogen but oxygen is the most important [16]. The effect of oxygen in molten-metal corrosion differs depending on whether the oxygen resides in the molten metal or solid metal [20]. When oxygen contaminants reside in the molten metal, corrosion proceeds by the dissolution of the solid metal into the molten metal. Oxygen in the molten metal melt reacts with refractory metals to form a corrosion product, which if is soluble in the melt, can accelerate corrosion [22].

Hoffman et al [23] report that the use of alloying elements such as zirconium and hafnium can improve the corrosion resistance of refractory metals [20,22]. These alloying elements form oxide layers of ZrO₂ and HfO₂ on the surface of refractory metals, are very stable and increase the threshold oxygen concentration needed for corrosion to occur [23]. Even though the solubility of refractory metals in molten Li is low, they can still be attacked by molten metal if the metals have high oxygen content. The oxygen concentration of niobium must not exceed a threshold level of 400 ppm Li in order to prevent penetration of the metal [20]. This observation of threshold concentrations was noted throughout the corrosion tests performed on refractory metals in different molten metals as reported by Hoffman et al [22]. This form of corrosion can thus be eliminated by minimizing the concentration of oxygen in the refractory metals [15]. Qian et al [18] that corrosion of Fe-Ni-Cr is also accelerated by impurities in molten Li. Nitrogen and carbon contaminants in molten Li react with Cr in the alloy metal to form Li₅CrN₅ and Cr₂3C₆. The depletion of Cr on the surface of the alloy results in the diffusion of Cr out of the alloy matrix which accelerates corrosion [18,20]. Molten Li also reacts with carbon in the alloy matrix to form Li₂C₂, a process called decarburization, which leads to intergranular corrosion. It is because of this corrosion mechanism that carbon steel is not considered suitable for molten Li containment [20,21].

![Figure 2 Solubility of different metals in molten lithium](image-url)
4. Considerations in the selection of a lining material

Information gathered from the literature discussed in previous sections can be used in selecting candidate lining material for the reactor vessel in the CSIR-Ti process. Based on the available information, Ni alloys perform better in molten LiCl environment but their efficiency decreases with increasing Fe and Cr content. However, in molten Li, Fe based alloys perform better with their performance degrading with increasing Ni content. This means that in an environment containing both molten Li and molten LiCl, Fe-Ni-Cr alloys will experience corrosion. However, with proper impurity control in the alloy as well as the molten Li and molten LiCl media, the alloys could be employed for long term service. It is important, however, that more extensive research be conducted to identify an optimum alloy composition beforehand.

The information gathered also shows that refractory metals can perform better in molten LiCl and molten Li provided there is low oxygen activity in the system. This implies, therefore, that to achieve optimal corrosion resistance, high purity refractory metals must be employed and proper control of impurities must be maintained in the system.

Table 1 below provides useful guidelines for selecting materials to use in molten Li and molten LiCl systems. These guidelines will help in ensuring that the lining material provides optimal performance and the environment is adequately controlled so as to avoid corrosion.

| Corrosion reaction | Guideline | Example |
|--------------------|-----------|---------|
| Direct dissolution | Lower activity of key elements | Reduce Ni in molten Li system, Reduce Fe and Cr in molten LiCl, Reduce carbon in Li and LiCl systems |
| Corrosion product formation | Lower reacting elements | Reduce Ni and Cr in Li system, Reduce Cr and Fe in LiCl system |
| Element transfer | Minimize transferred elements being | Reduce oxygen concentration in metal exposed to Li, Reduce the carbon content of metals exposed to Li |

5. Concluding remarks

Regardless of the growing interest in molten LiCl and molten Li, corrosion associated with these chemicals remains a significant concern. When these chemicals are used individually, their corrosion effect can be controlled more effectively but when both are present in a system, corrosion control becomes a significantly more complex task. This is due to the fact that some metals perform well in molten Li but poorly in LiCl. Some metals like refractory metals show great potential in both these environments but are sensitive to impurities. The use of refractory lining material demands therefore that both the metal and reagents have limited contaminant concentrations. Literature provides useful information and guidelines on the most suitable lining material but more research and experimental tests on different refractory metals and different grades of Fe-Ni-Cr alloys are needed to determine the optimum materials in both either case.
6. Acknowledgements

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7. References

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