CHAPTER-2

A REVIEW ON THE MATERIALS AND COATINGS FOR MOLTEN SALT AND URANIUM APPLICATIONS

This Chapter introduces the developmental aspects of pyrochemical reprocessing of spent metallic nuclear fuel. A brief overview of the carbon materials graphite, glassy carbon and pyrolytic graphite, their processing and applications to nuclear technology have been presented. Description of the ceramic coating materials and development of coating methods aspects with emphasis on plasma spray process are included. This Chapter reviews the materials and coatings developed for high temperature molten salt and uranium consolidation applications. The up to date literature on materials and coatings and their characterization and performance in molten salt and uranium applications are also covered in this chapter.

2.1 International experience on pyrochemical reprocessing

The evolution of nuclear technology encompasses the development of numerous methods for processing irradiated nuclear fuel. Separation techniques were initially developed in the 1940s and were applied to the separation of plutonium for military purposes [1]. Later, reprocessing of civilian irradiated nuclear fuel was introduced as a means of extending the uranium resources for future needs. The purpose of more complex fuel cycle schemes and the development of reprocessing methods are for achieving the goal of minimizing waste generation and reducing costs. This has resulted in renewed interest in dry reprocessing methods, known as “pyrochemical” processing [1]. Such processes have been studied in the
past by various countries. Pyrochemical processes attract strong interest, as they offer the potential for more compact (and hence, lower cost) facilities and the ability to handle irradiated nuclear fuel, cooled for shorter times [1]. Applications of pyrochemical processing for irradiated fuel vary from country to country. Some countries are oriented towards the treatment of thermal reactor fuel for the purpose of recycling and recovering actinides (primarily the transuranic elements) in fast spectrum reactors in order to provide sustainable nuclear energy systems. Other countries focused on fast reactor fuel cycle with processes being developed for treating metal [2], oxide [1] and nitride [3] fuels.

Electrochemical treatment of spent nuclear fuel using molten salt systems has progressed significantly over the last 20 years. Development, testing and demonstration operations have been performed with spent fuel for flowsheet development. This technology is expected to provide benefits over conventional aqueous options for treating spent nuclear fuel and enable the deployment of next generation nuclear power systems [4]. Pyrochemical processing has been implemented for the treatment of spent fuel from the Experimental Breeder Reactor-II (EBR-II) at Idaho National Laboratory since 1996 [5]. A successful demonstration of the technology was performed from 1996 to 1999 by the Department of Energy (DOE). Electrefining is the central technology for pyrochemical processing. The experiences on electrefining of spent fuels of EBR-II were summarized by Li et al. [5]. Central Research Institute of Electric Power Industry (CRIEPI), Japan started research and development work on metal fuel cycle in 1986, had initiated a joint study on pyrometallurgical technology with the United States DOE and showed progress in electrefining of metal fuel and treatment of wastes [6]. Japan has two proposals under consideration. One is to separate the minor actinides and long lived fission products from irradiated oxide fuels by
electrorefining after reducing them to metals and transmute them in critical or sub-critical reactors. The other is to use the nitride fuels in fast reactors and reprocess them by either molten salt electrorefining or nitriding in molten cadmium [1,6]. Research Institute for Atomic Reactors (RIAR) has used the pyroelectrochemical process for the production of tonnes of granulated UO$_2$ and (U,Pu)O$_2$ fuels for use as vipac fuel pins and for reprocessing enriched UO$_2$ and (U,Pu)O$_2$ irradiated fuels [1]. France has proposed to use pyrochemical processes for the separation of minor actinides and long lived fission products [1]. Korea Atomic Energy Research Institute (KAERI) has been developing pyroprocessing technology to handle the spent oxide fuel since 1990s [7].

Lee et al. [8] performed electrorefining using graphite as cathode in eutectic LiCl-KCl salt. The steel cathode proposed to be used in the electrorefiner was replaced by a graphite cathode, as graphite exhibited self-scraping behavior in which the electrodeposited uranium dendrite falls from the cathode surface on its own without any kind of further processing. The self scraping nature of graphite cathode would increase the efficiency of electrorefining process due to the elimination of mechanical scraping as well as the stripping of the cathode [8]. Recovery of uranium from the electrorefiner vessels containing a LiCl-KCl eutectic salt has been the on-going research work in the pyrometallurgical processing of used nuclear fuels for more than a decade. Usually, austenitic stainless steels are utilized for LiCl-KCl salt systems; however, the cadmium in the electrorefiner dictates an alternate material. A 2.25Cr-1Mo steel (ASME SA-387) was chosen due to the absence of nickel in the alloy, which has considerable solubility in cadmium. The vessel made up of 2.25Cr-1Mo was used as the electrorefiner vessel for the processing of EBR-II fuel. The corrosion of 2.25Cr-1Mo alloy in LiCl-KCl eutectic was evaluated to be uniform (i.e. non-localized corrosion) [9]. Without
cadmium, the selection of a material for the containment of LiCl-KCl salt would have been an austenitic stainless steel (304 SS or 316 SS) based on corrosion studies [10,11]. Evaluating the corrosion resistance of materials in molten chloride salts at high temperature is of prime importance for their use as equipment like electrorefiner and salt purification vessel in pyrochemical reprocessing plants. In order to overcome the corrosion of metallic materials in molten chloride environment, efforts were made to develop coatings on structural materials for various unit operations like salt preparation, electrorefining and cathode processing. Selecting materials and coatings for a critical application in reprocessing plants is a challenge where extended life of a material is demanded. Hence studies to identifying different materials and understanding their behaviour in molten salts by various research groups in the world become essential.

From international experience it is evident that pyrochemical reprocessing is leading technology worldwide and materials development for such critical applications is a challenging task. This chapter focusses on the corrosion behaviour of materials in lithium based molten chloride environment at high temperature, which is the medium for pyrochemical processing. Various materials were evaluated in molten chloride salts by different research groups in order to understand their corrosion behaviour, and the need for the development of coatings has been discussed in detail.

2.2 Carbon materials

Carbon exists in several physical forms which are known as polymorphs (or allotropes), with different names like graphite, diamond, lonsdalite, fullerene and others. The term “carbon material” is used to qualify such as carbon fiber, pyrolytic carbon, vitreous carbon and others [12]. These carbon materials have a sp² atomic structure and are essentially
graphitic in nature. Graphite is composed of series of stacked parallel layers with the trigonal sp\(^2\) bonding. The carbon atoms are arranged in a hexagonal lattice with a separation of 0.142 nm, and the distance between the planes is 0.335 nm [12]. Graphite materials such as pyrolytic graphite (PyG), carbon-fiber-carbon-matrix composites (carbon-carbon), vitreous carbon, carbon black and many other forms are actually aggregates of graphite crystallites and these all are called as polycrystalline graphites. The crystallite sizes in these graphites may vary considerably [12]. Carbon and graphite form a unique class of high temperature materials due to their strength and stiffness up to 2673 K under non-oxidizing environments [13]. The major disadvantage of carbon materials is their low oxidation resistance under oxygen containing environment. Because of this oxidizing nature, the strength of these materials reduce by nearly 50 % [13]. In the present thesis three kinds of carbon materials viz. graphite, glassy carbon (GC) and PyG have been studied for their possible applications in pyrochemical reprocessing. Hence, this chapter deals with the preparation of these carbon materials and their testing under various environments as reported in the literature.

Graphite materials can be prepared as dense or as very light body as well as highly anisotropic or as an isotropic material [14]. Graphite materials are prepared by heat treating a mixture of petroleum coke and coal tar pitch at high temperatures. The carbon product is further heat treated in an electric furnace in the temperature range 2773-3073 K to produce amorphous to crystalline graphite [13,14]. The manufacturing process steps were discussed in detail by Castro at al. [13]. Graphite possesses lubricity, strength, dimensional stability, thermal stability and ease of machining; a combination of these properties has led to its use in a variety of applications in industries. Its properties, through process modifications are tailorable to meet an array of design criteria for survival under extremely harsh environmental
operations. Carbon and graphite exhibit excellent resistance to the corrosive actions of acids, alkalies, and organic and inorganic compounds, an attribute that has attracted the use of graphite in process equipment [12]. Manufactured carbon and graphite parts exhibit varying degree of porosity. Because of their unique combination of physical and chemical properties, manufactured products of carbon and graphite are widely used in several forms in high temperature processing of metals, ceramics, glass, and fused quartz. Industrial carbon and graphite are available in a broad range of shapes and sizes. The resistance of graphite to thermal shock, its stability at high temperatures, and its resistance to corrosion permit its use as self-supporting vessels to contain reactive materials at elevated temperatures (1023–1973 K); self-supporting reaction vessels are used for the direct chlorination of metal and alkaline-earth oxides. Several grades of low density porous carbon and graphite are commercially available [15].

GC is an amorphous form of carbon with isotropic nature in properties [16,17]. GCs are produced by pyrolysis of thermosetting resins (eg. phenolformaldehyde) under controlled heating process at typical temperatures around 1173 to 1273 K [16-19]. The GC structure consists of randomly oriented hexagonal graphite-like layers [16,19] and it has very low porosity with moderately bulk density [17]. Depending on the preparation methods and process parameters the porosity can vary from near zero to several tens [19,20].

Synthetic form of graphite manufactured by chemical vapour deposition (CVD) is referred as PyG. It is a high purity form of carbon (< 1 atom % hydrogen). According to Kotlensky [21], thermal decomposition of hydrocarbon gases give rise to three products in the field of carbon namely (i) pyrolytic carbon (PyC), (ii) CVD carbon and (iii) PyG. All these names or terms refer to the same material. The two terms pyrolytic carbon and CVD carbon
are related to the deposition of carbon material by the pyrolysis of a hydrocarbon vapour. The term “PyG” is a particular high temperature form of PyC or CVD carbon. There are two ways to obtain PyG; one is deposition of PyC followed by graphitization at temperatures above 2273 K. In the second method deposition is carried out at temperatures above 2273 K. PyG has the following excellent desirable properties among other forms of synthetic graphite because of the highly oriented crystallinity present in the structure: (i) Its strength increases with temperature especially at high temperatures above 2773 K (ii) Greater oxidation resistance and (iii) Low porosity (high density) etc.. The main application of PyG is in the form of coatings, and also in the bulk form, by making the coatings sufficiently thick over the substrate and machining for different shapes [12]. A free standing object can be made after separating PyG from the substrate, with sufficiently thick deposition [22,23]. PyG can be deposited on the substrate up to a thickness of approximately 7 inches [23] and it can be deposited over moulded graphite, carbon fibers and porous carbon-carbon structures [12]. The microstructure [24], structural features and other properties [25] of PyG depend upon the deposition conditions [26]. PyG has been chosen as a coating material over graphite because it has greater oxidation resistance, chemical inertness and good thermal shock resistance and is stronger than normal graphite [22]. PyG has considerable technological importance as a coating as well as structural (container) material in the field of nuclear technology.

2.3 Application of carbon materials in nuclear technology

Carbon and graphite find wide ranging applications as electrode, refractories and crucible components, moderator and structural components in gas-cooled nuclear reactors, and air craft brakes, rocket engine components and nose tips in aerospace applications [13]. Application of graphite in aerospace and nuclear reactor demand high reliability and
reproducibility of properties, mechanical integrity of product and product uniformity [15]. Different forms of carbon materials are employed for various applications in nuclear technology.

PyG is used in the front and back end of nuclear fuel cycle. Triso-coated fuel particle is used in high temperature reactor. Each particle contains a kernel of uranium dioxide or uranium oxycarbide (UO$_2$ or UCO) of 500 to 800 μm in diameter. The confinement barrier is managed by means of a coating of ceramic multilayer [27]. PyG is one of the crystalline forms of carbon and it can be deposited on graphite for providing high temperature corrosion resistance in aggressive molten salt environments [28,29]. It is used as crucibles and as coating material on graphite crucibles in RIAR for fuel reprocessing in corrosive molten salt environment [28-30] and also as electrode material for the electrochemical reduction of oxides into metals in LiCl melt [31]. PyG crucible has been used as anode in the electrolysis process of pyrochemical method [32]. Corrosion studies carried out by Takeuchi et al. [29] on PyG and other ceramic materials like mullite and cordierite in molten NaCl-KCl salt (for oxide fuel reprocessing) at 1023 K for 24 h showed negligible corrosion rate (0.01 mm/y) under Cl$_2$ bubbling conditions. However, in Cl$_2$-O$_2$ (1:1) atmosphere in molten salt medium the corrosion rate was more than 0.5 mm/y. This clearly indicated that oxygen environment is not conducive to PyG [29]. The weight loss in PyG was insignificant compared to GC weight loss (0.5 wt%), when tested in molten fluoride environment at 813 K for the duration of 1-10 h and at 1268 K for about 1 h [20]. Magdziarz [33] investigated the thermal oxidation behaviour of general grade graphite, GC, pre-baked and pyrolytic carbon in air and nitrogen atmospheres at 833 K for application in molten salt based Fray-Farthing-Chen (FFC) electro reduction process and had recommended the use of GC and PyC as anodes for electro
reduction at lower temperatures because of their high resistance to oxidation compared to graphite and pre-baked carbon. GC is widely used as electrode and crucible material for various processes [34]. It was also used as anode crucible and as working electrode in electrochemical measurements in pure LiF-NaK-KF, LiF-NaK-KF-UO$_2$ and UF$_4$ melt [35].

Graphite crucibles are extensively used in pyrochemical reprocessing of metallic nuclear fuels as cathode processor material and casting furnace crucibles [36,37], liners [36] and as electrodes and tubes for chlorination at 973 K [30]. Graphite served as the crucible for cathode processing for the purpose of consolidating uranium from the cathode deposit comprising uranium, cadmium and 20-30 wt.% of salt [5]. Graphite crucible along with liner has been used for melting and purification of molten salt under chlorine atmosphere [38]. Bernardet et al. [39] carried out the interaction studies between nuclear graphite and graphite protected by a glassy carbon coating and a double coating of PyC/GC in molten fluoride salt. The behaviour of unprotected graphite was far from satisfactory after two days of immersion of graphite in molten salt at 773 K. The best way of protecting graphite surface, with maximum inertness towards molten salt, has been obtained by providing a double coating of PyC/GC. The importance of PyC/GC coating for molten salt applications was highlighted in their study. Further, the coating layer exhibited perfect adhesion on the surface of nuclear grade graphite and a very weak adherence towards the molten salt [39].

Selection of materials is one of the critical issues in the accelerator driven transmutation technology (ADTT) [20]. GC, PyG and Hastelloy B are considered as candidates for structural materials of the ADTT systems. The interaction of molten fluoride salt with these materials in a bath of the molten salts either as one-component LiF (100%) at the temperature of 1268 K or in a mixture of LiF (46.5 wt%) + KF (42 wt%) + NaF (11.5
wt%) (FLiNaK) with a melting point of 813 K has been investigated [20,40]. Pyrolytic graphite was found to be chemically intact; corrosion attack was evident on GC and particularly on the surface of Hastelloy B [20,40]. Different carbon allotropes and metallic foils (Ni, Ti, V and Mo) were exposed to molten LiF based salt mixture at 813 K (1 to 10 h) and 1268 K (1 h) and their weight loss (%) measured after the corrosion test by Vacik et al. [40] are listed in Table 2.1. Very low values of corrosion were observed for GC and PyG compared to metallic foils [40].

**Table 2.1 Weight losses in carbon materials and metallic foils in molten LiF based salt**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>LiF 995°C, 1 h</th>
<th>LiF+KF+NaF 813 K, 1 h</th>
<th>LiF+KF+NaF 813 K, 5 h</th>
<th>LiF+KF+NaF 813 K, 10 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>0</td>
<td>0</td>
<td>~11</td>
<td>~0.5</td>
</tr>
<tr>
<td>PyG</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Reactor graphite</td>
<td>~24</td>
<td>~11</td>
<td>dissolved</td>
<td>-</td>
</tr>
<tr>
<td>Nickel</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>~0.5</td>
</tr>
<tr>
<td>Titanium</td>
<td>~52</td>
<td>~42</td>
<td>dissolved</td>
<td>-</td>
</tr>
<tr>
<td>Vanadium</td>
<td>~35</td>
<td>~15</td>
<td>~23</td>
<td>dissolved</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>~50</td>
<td>~12</td>
<td>~26</td>
<td>dissolved</td>
</tr>
</tbody>
</table>

Molten salt reactor systems demand structural materials to effectively resist corrosion by fluoride salt mixtures. In order to select the best suited materials for molten salt reactor extensive corrosion studies were carried out with graphite in molten fluoride salt up to 1000 h exposure at 978 K. After corrosion test, graphite indicated penetration of salt to a great extent through the available pores. [41]. Development of PyC coating on nuclear grade graphite is a promising method for to resist the attach of fluoride salt its application in Molten Salt Reactor
Pyrolytic carbon (PyC) coatings were deposited on nuclear grade graphite (IG-110) by thermal decomposition of methane at 2103 K. The PyC coating was pretty dense and anisotropic with nanopores. Helium gas permeability into nuclear grade graphite was significantly decreased after PyC coating. These results indicate that the PyC coating is dense and pore free to protect the nuclear graphite against the permeation of molten fluoride salts and the diffusion of fission gases [42]. These studies recommended the use of impervious grades of graphite for molten salt applications in order to control corrosion. Graphite is also used as moderator in molten salt breeder reactors (MSBR) as it resists radiation and tolerates fission product accumulation. The type of graphite to be used in the MSBR should not undergo any chemical reaction with molten fluoride mixtures [43].

2.4 Molten salt corrosion behaviour of structural materials

The specific type of corrosion of metals and alloys in molten salt at high temperature is known as hot corrosion [44]. Corrosion reaction in molten salts is a fairly complex phenomenon. Loss of material after corrosion test could be attributed to the corrosion reaction and homogeneous or heterogeneous attack on the surface [45]. Material’s behaviour in molten salt was studied mainly by gravimetric method or by weight change measurements and subsequent surface examination/characterization [45]. Uniform metal oxidation and dissolution is a common form of molten salt corrosion. Selective leaching is very common at higher temperatures, while pitting and crevice corrosion are seen at lower temperatures [46]. All the forms of corrosion observed in aqueous systems including stress-assisted corrosion, galvanic corrosion, erosion-corrosion and fretting corrosion have occurred in molten salts. Many of the principles that apply to aqueous corrosion, such as anodic reactions leading to metal dissolution and cathodic reduction of an oxidant also apply to molten salt corrosion.
The corrosion process is mainly electrochemical in nature because of the excellent ionic conductivity of most of the molten salts [45,46]. Even though the corrosion mechanism is similar, there are major differences between molten salt and aqueous corrosion as listed in Table 2.2. The differences arise mainly from the fact that molten salts are partially electronic and ionic conductors, which allows reduction reactions to take place in the melt as well as at the metal-melt interface. Molten salt systems operate at higher temperatures than aqueous systems, and cause different forms of corrosion attack. High-temperature corrosion in molten salts often results in selective dissolution and internal oxidation [46].

Table 2.2 The difference between aqueous and molten salt corrosion mechanisms.

<table>
<thead>
<tr>
<th>Aqueous corrosion</th>
<th>Molten salt corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple anodic and cathodic reactions</td>
<td>Complex situation with several oxidants</td>
</tr>
<tr>
<td>Passive state can be easily maintained (e.g. SS, Ti)</td>
<td>Passive state maintenance is less promising due to salt</td>
</tr>
<tr>
<td>Pourbaix diagram can be used to understand M-H2O corrosion (Potential-pH)</td>
<td>Basicity diagrams can be used to understand M-salt corrosion (Potential-pO2⁻)</td>
</tr>
<tr>
<td>Anodic reaction involves dissolution of metal and formation of metal oxides</td>
<td>Anodic reaction involves dissolution of metal and formation of salt times</td>
</tr>
<tr>
<td>Cathodic reaction involves reduction of species</td>
<td>Cathodic reaction is complicated and depends on oxidants and trace impurities</td>
</tr>
</tbody>
</table>

Evaluation of molten salt corrosion is essential to understand the material behaviour under aggressive molten salt environment. AISI 316L stainless steel (SS) was envisaged as a candidate material for the fabrication of components for various unit operations in pyrochemical reprocessing [47]. The corrosion of 316L SS after immersion in molten LiCl-KCl salt up to 250 h at 773 K under UHP argon resulted in sever corrosion and formation of
voids. Enrichment of Cr toward the top surface and underlying Cr-depleted layer with voids was observed in exposed 316L SS [47]. The thickness of the degraded layer containing voids increased with increase in the duration of exposure from 25 to 250 h and the spallation of chromium-rich compound could be seen in the sample exposed for 250 h. From international experience, Cr-Mo steels were considered for use as container material as molten Cd present in the electrorefiner protects the steel container [48]. The percentage weight loss values of 2.25Cr-1Mo and 9Cr-1Mo exposed to molten LiCl-KCl salt at 873 K indicated that 2.25Cr-1Mo suffers more corrosion attack when compared to 9Cr-1Mo steel. Hence, 9Cr-1Mo steel is the most preferred material than 2.25Cr-1Mo steel because of its good corrosion resistance in chloride environment and high temperature properties. Thus, 9Cr-1Mo is proposed as an alternative candidate material for electrorefiner vessel in pyrochemical reprocessing plant [49]. It has been widely accepted that Nickel-rich alloys suffer less from corrosion attack in chlorine containing environment than carbon steels and stainless steels [50]. Therefore, INCONEL alloys were considered as candidate materials for the fabrication of transfer lines of salt purification system where Cd free molten LiCl-KCl salt is handled [49]. INCONEL (600, 625 and 690) exposed for 500 h at 873 K exhibited weight gain due to the formation of adherent corrosion products on the surface of the sample. Microstructural analysis of INCONEL (600, 625 and 690) exposed for 100 h showed two regions: corrosion attacked regions rich in Cr and Fe and Ni rich matrix adjacent to the corrosion products. Accidental ingress of moisture and oxygen will aggravate the corrosion of structural materials used and hence the materials selected should withstand such aggressive environment. A study was initiated to understand the corrosion behaviour of 316L SS, INCONEL alloy (600, 625 and 690), electroformed (EF) Ni and EF Ni with Ni-W coating in molten LiCl–KCl at 673, 773
and 873 K for 2 h in the presence of air and the corrosion resistance was found to be in the following order: INCONEL 690 > INCONEL 600 > INCONEL 625 > EF Ni with Ni-W coating > EF Ni > 316L SS [49,51]. Preferential leaching of Cr from the surface and formation of Cr rich corrosion products appeared to be the common mechanism of corrosion for all the alloys exposed to molten LiCl-KCl salt [49].

Corrosion is an important issue during salt purification as the high temperature molten salt picks up oxygen and moisture and salt purification is carried out by passing chlorine gas which is highly corrosive in nature; therefore, the effect of Cl₂ on the INCONEL alloys needs to be understood. INCONEL 600, 625 and 690 base and weldments were tested in molten LiCl-KCl eutectic salt at 873 K for 30 min under Cl₂ gas [52]. INCONEL 690 exhibited better corrosion resistance than INCONEL 600 and INCONEL 625. INCONEL welds exhibited marginally higher corrosion rate than the base alloy [52]. Beryllia (BeO) crucibles are used as the container for liquid cadmium cathode as they are highly resistant to attack of molten salt and were not even wetted by uranium [48]. Hosoya et al. [53] studied the corrosion behaviour of Ni-based superalloy, Hastelloy-X and refractory metals (Ta and W) in molten NdCl₃-NaCl-KCl salt at 773 -1023 K for 60 min. Hastelloy-X showed no evidence of attack and refractory metals (Ta and W) retained glossy surfaces even after immersion test. Tantalum, tungsten and Hastelloy-X had sufficient corrosion-resistance against molten chlorides when moisture and oxygen were appropriately removed [53]. Indacochea et al. [54,55] tested tantalum, 316 L SS, 422 SS, 430 SS and 2.25 Cr-1 Mo steel in molten LiCl-3.5 wt % Li₂O and 1 wt % Li₃N salt saturated with Li metal at 998 K for 30 days whereas 304 SS, 316L SS, INCONEL 600 and INCONEL 625 were tested in molten LiCl-3.5 wt % Li₂O and 1 wt % Li₃N salt saturated with Li metal at 923 K for 6 days under argon and argon + 10 % O₂
atmosphere. Corrosion attack was minimum in the case of materials tested under pure argon as the cover gas. Corrosion was severe when a cover gas of argon + 10 % O₂ was used, even after the test temperature was reduced to 923 K and exposure time was shortened to 6 days. Oxygen gas plays a crucial role in corrosion and not as an oxide. Types 316L SS and 304 SS had similar corrosion behaviour even with the presence of Mo in 316L SS. The 316L SS welded specimen was severely corroded and intergranular attack was detected in the heat affected zone despite the low carbon content of this steel. INCONEL 600 showed the best corrosion performance among all the alloys tested and INCONEL 625 performed poorly as a consequence of higher amount of Mo and Cr present in the alloy [55].

The high temperature refractories ZrN and HfN are known for their chemical inertness in extreme corrosive environments. Periasamy et al. [56] investigated the compatibility of ZrN and HfN in molten salt mixture (28.5% LiCl–36.3% KCl–29.4% NaCl–5.8% UCl₃) at 998–1173 K for 4–485 h. Both ZrN and HfN experienced weight loss under all experimental conditions due to the formation of volatile products and electrochemical dissolution. Formation of volatile Zr–Cl and Hf–Cl products was believed to occur due to the reaction of the nitrides with Cl₂(g) or Cl⁻, which in turn was generated by the reaction of UCl₃ species present in the salt with oxygen [56]. Effect of uranium, plutonium and trans-uranium elements on the corrosion behaviour of ceramics was required to select them as high corrosion resistant materials for RIAR process. For this purpose investigations using simulated trans-uranium elements added molten salt was carried out [29]. Takeuchi et al. [29] tested SiC, Si₃N₄, BN, AlN, ZrB₂, Al₂O₃, Y₂O₃, Al₆Si₂O₁₃, Mg₂Al₃(AlSi₅O₁₈) and pyrolytic graphite in 2CsCl-NaCl molten salt and its vapour phase at 923 K under Cl₂ + O₂ gas. The corrosion resistances of these ceramics were excellent and were less than 0.1 mm/y. No cracks were observed on the
materials and mechanical strength did not drop remarkably after 480 h of corrosion test under Cl₂+O₂ atmosphere. Pyrographite suffered from severe damage by the effect of oxygen in molten salt. Silicon nitride, mullite and cordierite were promising for severe corrosion environment, particularly in RIAR process [29].

Since metallic and carbon materials undergo accelerated corrosion under severe corrosive environment and high temperatures, the vessels and crucibles made up of these materials need to be coated with corrosion resistant ceramic materials by efficient and flexible processes. It is also necessary to identify and develop of high temperature materials and coatings which are amenable to remote handling operations under highly aggressive and radioactive molten salt atmosphere.

2.5 Materials and coatings

In the process of selection of appropriate coatings for any application the following requirements should be satisfied: (1) The coating must have adequate mechanical–thermal resistance, (2) Thermophysical parameters of coating and substrate must be nearly identical, (3) Coating must have minimum chemical interaction with the environment, (4) Adhesion with substrate should be strong, (5) Possibility of multiple restoration of coating and (6) Coating material should be relatively economical and commercially available. According to Shifler [57], the performance of high temperature coatings are chosen depending on the following important parameters: (1) the environment, (2) temperature, (3) quality control of the coating application, (4) coating structure and chemistry, (5) fuel contaminants and (6) nature of substrate. Before selecting a material for high temperature molten salt applications, the thermodynamic stability of the coating material at the temperature of interest should be assessed. Based on the Gibbs energy data SiO₂, ZrO₂, BeO, ZrO₂-SiO₂ and yttria stabilized
zirconia were found to be the candidate materials, [28,47,58-60] for molten salt environment at temperatures up to 1273 K. Various ceramic materials used for developing thicker coatings (i.e. thermal barrier coatings), their properties, advantages and limitations were listed by Cao et al [61].

High purity alumina coatings are widely used for insulation purpose of metals and alloys. Alumina composites rather than pure Al$_2$O$_3$ have certain advantages. Ananthapadmanaban et al. [62] reported that TiO$_2$ with a lower melting point effectively binds alumina grains, contributing to high density. Alumina powder with the addition of TiO$_2$ in the range of 3, 13 and 40 wt% is widely used for coating applications using thermal spray process [63-65]. Increasing TiO$_2$ content in the sprayed powder leads to a decrease in the melting temperature of the alumina-titania coating, resulting in the tendency to diminish the porosity [64] and increasing the fracture toughness of the coating [66,67]. The percentage of porosity of the 60/40 Al$_2$O$_3$-TiO$_2$ mixtures was lower than other compositions (i.e. 97/3 and 87/13). The microhardness of Al$_2$O$_3$-TiO$_2$ composite coatings depends essentially on their composition. The hardness decreased linearly with increase of TiO$_2$ content or decreasing alumina content [66,68]. The doping of TiO$_2$ into alumina could partially stabilize the $\alpha$-phase of Al$_2$O$_3$ [63]. Alumina-titania coatings are excellent candidates for providing protection against abrasive wear, and are resistant to high temperature erosion. Such coatings are desirable for electrical insulation and anti-wear applications; for example in protective coatings for sleeve shafts, thermo-couple jackets, pump shafts etc. In addition to exhibiting good wear; these coatings exhibits corrosion and thermal shock resistance [69].
Porosity of Al$_2$O$_3$-40 wt% TiO$_2$ was reduced when agglomerated powder was used which also improved the homogeneity of the coating, owing to the formation of a new compound, Al$_2$TiO$_5$ [70]. Al$_2$O$_3$ and TiO$_2$ react together to form Al$_2$TiO$_5$, in accordance with the Al$_2$O$_3$–TiO$_2$ phase diagram shown in Fig. 2.1 [70]. The formation of this compound in the coating process improves the coating performance with respect to corrosion and thermal shock resistance. Based on the experience available in literature and its beneficial properties Al$_2$O$_3$-40wt% TiO$_2$ coating has been selected for the current study.

The performance of zirconia is reported to be satisfactory among the materials presently used for thermal barrier coatings. Zirconia (ZrO$_2$) has high melting and boiling points; it exhibits polymorphism with three stable phases up to its melting point of 2690°C [71]. The following characteristics of pure zirconia are evident from the phase diagram shown in Fig. 2.2 [72]: Melting point: 2690°C/2963 K; Cubic (C) to tetragonal (T) phase
change: $2370^\circ$C/ 2643 K; Tetragonal (T) to monoclinic (M) phase change: $1170^\circ$C/ 1443K.

The details of the phase transitions in ZrO$_2$ are listed in Table 2.3 [73].

![Phase diagram of ZrO$_2$–Y$_2$O$_3$][72].

**Table 2.3** The details of the phase transition in ZrO$_2$ [73]

<table>
<thead>
<tr>
<th>Parameters for the phase transition in ZrO$_2$</th>
<th>Monoclinic</th>
<th>Tetragonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
<td>$C_{2h}^5$</td>
<td>$D_{4h}^{15}$</td>
<td>$O_{h}^5$</td>
</tr>
<tr>
<td>$T_a^{(heating)}$</td>
<td>$1150^\circ$C</td>
<td>$2370^\circ$C</td>
<td></td>
</tr>
<tr>
<td>$T_c^{(cooling)}$</td>
<td>$900^\circ$C</td>
<td>$2355^\circ$C</td>
<td></td>
</tr>
<tr>
<td><strong>Order</strong></td>
<td>4</td>
<td>1st</td>
<td>1st</td>
</tr>
<tr>
<td><strong>Lattice parameters</strong></td>
<td>a=5.142 Å</td>
<td>a=3.653 Å</td>
<td>a=5.272 Å</td>
</tr>
<tr>
<td></td>
<td>b=5.206 Å</td>
<td>c=5.293 Å</td>
<td>(2400$^\circ$C)</td>
</tr>
<tr>
<td></td>
<td>c=5.313 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\beta=99^\circ18'$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(30$^\circ$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Monoclinic ZrO$_2$ is seldom used in high temperature applications because of its polymorphic transformation accompanied by dimensional changes [74,75]. The tetragonal-to-monoclinic
phase transformation is martensitic in nature because it does not require diffusion and occurs by small displacement of atoms in the structure. The transformation occurs on cooling zirconia from high temperature and it involves 3-5% volume increase. The volume change induces a significant shear strain, as high as 10%, in the structure, affecting the integrity of the coating [71]. Alloying zirconia with other oxides such as CaO, MgO, Y₂O₃, CeO₂, Sc₂O₃ and In₂O₃ inhibits the phase transformation, stabilizes the high-temperature phase and eliminates the volume change [76,77,71]. Among these stabilizers, the most commonly used is yttria, because of the long term stability of the resulting oxide. The optimum content of approximately 6-8 wt % yttria stabilizer in zirconia exhibits longer lifetime because of the presence of maximum amount of non equilibrium, “non transformable” tetragonal phase formed during the quenching process as indicated in the phase diagram (Fig. 2) [71,78,79]. Significantly lower yttria contents do not inhibit the transformation to monoclinic phase, while higher levels stabilize the cubic phase which lacks adequate strength, thermal shock resistance and toughness. As a result, 7 wt % yttria stabilized zirconia (named as 7YSZ) has become the industrial standard [71].

Coatings are applied to high temperature components to resist environmental degradation [80]. According to Heath et al. [81] four important critical properties to protect components from high temperature/molten salt corrosion are: chemistry of the coating, coating thickness, adhesion and thermal expansion co-efficient of coating and base material. Thermal spray coatings find extensive applications in aerospace, chemical, waste incineration, power generation, pulp and paper, petroleum, infrastructure, medical prosthesis and automotive industries for protection against corrosion [81,82]. The application of thermal spray coatings for reprocessing of nuclear fuel was initiated around 1990s and widely used
now for the molten salt environment. Thermal spray coating represents a group of processes in which plasma spray is one of the versatile and widely used processes [71,78,83]. The principle behind the thermal spray is to melt the material feedstock (wire or powder), accelerate the melt to impact on a substrate where rapid solidification and deposit buildup occur. Thus, a heat source and a means of accelerating the material are required. This is pictured schematically in Fig. 2.3 [84].

![Thermal spray process diagram](image)

**Fig. 2.3. A schematic overview of thermal spray process** [84].

Thermal spray technique was recommended for ceramic coatings on graphite and graphite ceramic systems [85,86]. The most important advantage of thermal spray coatings is the possibility of on-site application and repair of components, given a sufficient accessibility for the sprayer and its equipment [81]. Plasma spraying is one of the extensively used thermal spray processes because of the ability to deposit several metallic and ceramic materials with high deposition rate [87,88] of coating to reduce high temperature oxidation and molten salt corrosion. In economical point of view, cost performance ratios of thermal sprayed coatings are of special interest [81]. Plasma spray process is capable of producing micrometer range thick coatings with deposit efficiency < 50 to 90% and deposit rate <3 kg/h to 50 kg/h for reproducible and durable coatings [81]. Plasma spray process is a straightforward technique scaling from laboratory experiments to industrial production [89]. All materials can be
sprayed by plasma spray process on any type of substrate [90]. The adhesion of ceramic coatings to metallic and non-metallic materials is poor. For improving the adhesion of ceramic coatings to the substrates a bond coat was used as an intermediate coating. Many review articles [91,92] provide extensive details of plasma spray process in the literature. Therefore, detailed discussion on the plasma spray process is not attempted, but the performance of plasma sprayed coatings in molten salt is focused in the following section, as it is of relevance to the present work.

YSZ (7-9 wt%) with an intermediate metallic bond coat (NiCrAlY) is considered as one of the options to protect the structural materials (viz. type 316L SS) of salt purification vessel. Corrosion studies carried out on YSZ coated 316L SS in molten LiCl-KCl salt at 773 K for 500 and 1000 h exhibited better corrosion resistance compared to uncoated 316L SS [47,58]. Weight loss studies indicated that the percentage of weight loss for 500 and 1000 h exposed samples was negligible and no significant degradation or penetration of salt across the coating was observed [58]. Partially stabilized zirconia (PSZ) coated on 9Cr-1Mo samples and tested in molten LiCl-KCl salt up to 2000 h showed marginal increase in weight, but the coating exhibited large number of cracks and buckling [49]. The results indicated that premature spallation of PSZ coating on 9Cr-1Mo could have occurred due to accidental ingress of oxygen and moisture [49]. YSZ and Al₂O₃ coatings on Inconel 713LC by plasma spraying were tested in molten LiCl-3 wt % Li₂O salt at 923 K in a mixed gas of Ar-10 wt% O₂ for 24 to 168 h. The corrosion rate for the Al₂O₃ coating was 5.8 x 10⁻² µm/h while for YSZ coating, it is nearly zero. A porous reaction layer was formed due to reaction of Al₂O₃ with Li₂O. The dense amorphous reaction layer on the surface of the YSZ coating offered better protection and provided an effective barrier against the LiCl-Li₂O molten salt [59].
Plasma sprayed ZrO\textsubscript{2} and ZrO\textsubscript{2}-SiO\textsubscript{2} coatings on graphite and pyrolytic graphite coating on high density graphite by chemical vapour infiltration were tested in NaCl-KCl-CsCl-UO\textsubscript{2}Cl\textsubscript{2} (5 wt % U) for 6 h at 873 and 923 K under Cl\textsubscript{2} +O\textsubscript{2} gas. Based on the corrosion results, the life time of ZrO\textsubscript{2} is shortest compared to ZrO\textsubscript{2}-SiO\textsubscript{2} and pyrolytic graphite while the lifetime of ZrO\textsubscript{2}-SiO\textsubscript{2} was estimated to be three times longer than that of ZrO\textsubscript{2} and pyrolytic graphite. ZrO\textsubscript{2}-SiO\textsubscript{2} material was found to be the most promising compared to pyrolytic graphite [28].

ZrO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}-Cr\textsubscript{2}O\textsubscript{3} coatings on IN713LC by plasma spraying were tested in molten LiCl-3 wt% Li\textsubscript{2}O salt at 948 K in a mixed gas of Ar-10% O\textsubscript{2} for 216 h. Superior corrosion resistance shown by ZrO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}-Cr\textsubscript{2}O\textsubscript{3} top coat was attributed to their chemical and thermal stability [60,93]. Adhesion and chemical stability tests were conducted on graphite coated with TiN and TiC by chemical vapor deposition by Maiya et al. [94]. The coated specimens were exposed to a corrosive molten salt CaCl\textsubscript{2} and a liquid metal alloy (Zn-10 wt.% Mg) at 1073 K for 168 h to determine the corrosion resistance. No reaction discontinuity of coatings along the interface was detected by scanning electron microscopy or energy-dispersive X-ray spectroscopy. TiN and TiC coatings on graphite were chemically stable in corrosive and reducing molten salt and liquid metal alloy baths in addition to displaying good adherence. It is apparent that graphite coated with TiC and TiN by chemical vapour deposition is a promising container material for pyrochemical processing [94]. High density graphite substrates have been coated with Y\textsubscript{2}O\textsubscript{3} using pulsed laser deposition technique and were exposed to molten LiCl-KCl salt at 873 K. The results revealed that Y\textsubscript{2}O\textsubscript{3} coating offers better compatibility and provides protection to high density graphite from the attack by molten chloride salt [95].
2.6 Coatings for heavy metal consolidation application

For various applications, uranium and its alloys are generally melted by induction heating in ceramic coated graphite crucibles under vacuum [96]. Graphite has been the proposed crucible material for such applications, because of its high-temperature strength and resistance to thermal shock. The crucible material for processing of molten uranium should satisfy the following requirements: (a) withstand the thermal cycle, (b) ease of release of uranium ingot, (c) should not interact with and contaminate the ingot, (d) should be reusable and (e) preferably does not require extensive preparation methods. As carbon readily reacts with uranium, it must be coated to prevent reaction with uranium. Even very little contact between the molten uranium and graphite causes an interaction that lead to the ingot being firmly stuck with the crucible. This usually requires destruction of the crucible to recover the ingot. Other crucible materials such as ceramics and metals have also been tested due to the stringent requirements. Owing to the presence of 20-30 wt % chloride salt along with uranium deposited in the cathode, it is all the more difficult to select materials for such processes [97]. Holcombe et al. [98] estimated the chemical reactivity of different ceramic oxide coating materials with both uranium and carbon based on the temperatures of interaction and summarized the oxide/uranium interactions. Al₂O₃, Y₂O₃ and ZrO₂ coatings obtained by sponging, brushing or spraying on graphite were tested under cathode processor operating conditions up to 1573 K under vacuum. Al₂O₃ coating failed to adhere well to graphite, yttria was attacked by the chloride salts and zirconia coating resulted in degradation [97]. Plasma sprayed multilayered coatings on graphite crucibles also gradually deteriorated and flaked off due to lower adhesion strength [97]. Cho et al. [99] employed plasma sprayed alumina and YSZ top coated on graphite for cathode processor application, not only to reduce the reaction
between uranium and graphite but also to reduce the interaction between molten salt containing UCl\textsubscript{3} and graphite. Ceramic lined crucibles were developed based on the experience with zirconia coatings. Zirconia based castable liner (78 wt% ZrO\textsubscript{2}, 20 wt% Al\textsubscript{2}O\textsubscript{3} and 2 wt% C) was developed on graphite crucible for testing under cathode processor operating conditions at 1473 K (< 100 Pa). Ceramic liners improved the performance of graphite crucible for the separation of salt during uranium processing [100].

As Y\textsubscript{2}O\textsubscript{3} is highly compatible to molten metals and salts at high temperatures and because of its high melting point and thermal stability, Y\textsubscript{2}O\textsubscript{3} was used as coating material for high temperature corrosive environment [101,102]. Y\textsubscript{2}O\textsubscript{3} coating is reported to be stable with graphite up to 1873 K without initiation of a reaction with graphite substrate [102]. Plasma sprayed Y\textsubscript{2}O\textsubscript{3} coatings on graphite were tested in molten uranium at 1573-1773 K for 30 min. Superior corrosion protection was observed up to 1573 K and above, but it became less satisfactory above 1723 K when applied directly on graphite due to the interaction of graphite with yttria at that temperature [96]. The performance of yttria coating was improved using a bilayer of Nb/ZrO\textsubscript{2} in between Y\textsubscript{2}O\textsubscript{3} and graphite up to 1773 K. The Nb/Y\textsubscript{2}O\textsubscript{3} coating on graphite crucible was used for seven melts at 1723 K without degradation of coating [96]. Padmanabhan et al. [102] investigated the reaction of Y\textsubscript{2}O\textsubscript{3} with uranium using a thermogravimetric TG/DTA analyser at 1473 K for 2 h under helium gas. There was absolutely no reaction of Y\textsubscript{2}O\textsubscript{3} coatings with molten uranium. Sticking of uranium pellet to Y\textsubscript{2}O\textsubscript{3} buttons was also not observed by them. Based on these results, Y\textsubscript{2}O\textsubscript{3} coating was plasma sprayed on tantalum for processing liquid uranium at 1573 K and tested for 80 h [103]. The Y\textsubscript{2}O\textsubscript{3} coating exhibited excellent corrosion resistance against liquid uranium. No reaction products were observed at the uranium-Y\textsubscript{2}O\textsubscript{3} interface. Instabilities leading to crack
and spallation of the coating were not observed indicating that the coating had good adhesion to the tantalum substrate [103].

Kim et al. [104] used plasma spray process to deposit HfN, TiC, ZrC, and Y₂O₃ coatings on niobium substrate and conducted melt interaction studies with U-Zr fuel at 1823 K for 15 min under vacuum. HfN and Y₂O₃ didn't form significant reaction layers between U–20wt % Zr melt and the coating layer. Y₂O₃ coating was found to be the most promising coating material compared to HfN, TiC and ZrC for re-usable crucibles for metallic fuel processing due to good thermal compatibility with U–20 wt.% Zr melt. Thermal cycling tests were conducted up to 1723 K at a rate of 193 K/min, held for 30 min, followed by cooling to room temperature. The results indicated that HfN, TiC, ZrC, and Y₂O₃ coatings possessed good thermal cycling characteristics with the development of only a few interconnected cracks in ZrC and no interconnected cracks in the other materials even after 20 cycles, exhibiting a good thermal shock resistance [104]. Al₂O₃ substrates coated with TiN by ion beam assisted deposition technique were tested with uranium at 1773 K for 4 h under a vacuum of 10⁻⁴ Pa. TiN thin film was appeared to protect alumina, because no reaction between TiN and uranium was observed even at 1700 K. However, TiO₂ was formed at the interface of substrate-coating because of the reaction between TiN and Al₂O₃ [105]. HfN plasma sprayed on niobium crucible was tested under cathode processor conditions (heated to 1473 K at pressure less than 100 Pa) and coated crucibles were found to perform for 15 runs with uranium and salt. No apparent degradation on the crucible or its HfN coating was observed. No difficulties were encountered on ingot dumping [106]. Holcomb et al. [107] used aluminium titanate (Al₂TiO₅) coated titanium crucible for melting uranium at 1413-1523 K for 5 to 45 min, under a vacuum of < 1 x 10⁻⁵ torr. No cracking and spallation of Al₂TiO₅
coating was observed after melting, and the pellets could be detached easily from the crucibles. Brown coloured uranium oxide films were observed on the surface of coating due to the slow and time dependent reduction of aluminium titanate by molten uranium. Uranium titanate was not detected probably due to its unstable nature above 1313 K [107]. BeO crucible showed good chemical stability with process materials and could withstand thermal stresses of the process cycle. BeO crucibles are expected to provide reliable multi-use in addition to avoiding special preparation procedures [97]. Nevertheless, because of its high toxicity, usage of BeO coatings or its substrates is avoided. Reaction of lanthanum phosphate (LaPO₄) with uranium evaluated by differential thermal analysis at 1473 K for 2 h under helium gas showed no reaction between molten uranium and LaPO₄. The chemical stability of LaPO₄ with molten uranium and its stability against hydration reaction indicated its usefulness for molten uranium handling as well as thermal barrier applications [108]. Refractory oxides (Y₂O₃), carbides (NbC, VC, ZrC), nitrides (AlN, NbN, TaN, ZrN, VN, TiN) and sulfides (CeS) applied quartz and refractory metals were examined as mould coating materials for casting metallic fuel of IFRs [109]. Sessile drop tests were employed to study the interaction between ceramic coatings and molten U-10 wt% Zr at 1823 K. Among these coatings NbC, TiN and Y₂O₃ were found to be non-wetting with U-10%Zr; however, Y₂O₃ coating alone completely avoided adhesion of the fuel [109]. Coating materials such as CaO, ThO₂, Er₂O₃, MgO, HfO₂, Al₂O₃ and BeO plasma sprayed on W-Re, W, AlN, TiN, ZrB₂ and TiC were tested for their compatibility in cathode processor operation in order to identify a durable coating which would facilitate easy ingot release, minimize contamination and avoid loss of uranium metal. However, these coatings did not perform up to the required level of satisfaction [100].
For the purpose of corrosion protection, nanostructured coatings have been developed on structural materials for reprocessing applications [110]. Nitrides possessing high hardness, melting point and thermodynamic stability against reactive materials and molten LiCl–KCl salts have greater potential for coating graphite crucibles [111]. Gibb’s free energy values calculated for the reactions of TiN, ZrN and HfN with uranium from 373-1773 K indicated that these nitrides are stable in molten uranium [111]. Nanocrystalline TiN, ZrN and Ti–Si–N coatings were developed by DC/RF magnetron sputtering on high density graphite disc and crucibles for uranium melting experiments [111]. No significant coating detachment was observed after blank run and with uranium melting even at a very high heating rate of 358 K/min. TiN and Ti-Si-N coating appeared to offer better stability in comparison to ZrN [111]. Nanostructured thin film yttria was coated by pulsed laser deposition (PLD) on plasma sprayed thick Y₂O₃ coatings to seal and fill up the pores and cracks generated on the surface of the sprayed coatings in order to improve the performance of coatings on moulds and crucibles for handling molten uranium [101]. Uranium melting experiments were conducted on Y₂O₃ coated HD graphite crucibles by pulsed laser deposition at 1623 K for 20 min [112]. Phase identification by XRD revealed only cubic Y₂O₃ phase and peaks corresponding to uranium were absent. No detachment of coating was observed after uranium melting [95,112].

2.7 Post treatments on plasma sprayed coatings

The presence of porosity and microcracks in plasma sprayed coatings is a drawback and these may cause corrosion of the substrate on prolonged exposure to molten salts. The microstructure of plasma sprayed coatings can be modified by post treatments [113]. The commonly used post spray treatments for thermal spray coatings to protect from different corrosive environments are: chemical/physical (organic sealing, aluminizing and chromizing),
thermal (fusion, heat treatment, diffusion, recrystallization, laser glazing and hot isostatic pressing) and mechanical (machining, grinding, shot peening and polishing) treatments [114]. Heat treatments induce grain growth, initiate precipitation and interlamellar porosity will change to spherical porosity [92]. Among the four approaches proposed by Jones [115], to mitigate the corrosion of thermal barrier coatings one of them is laser based glazing or melting or sealing of coating to obstruct the penetration of salt into the coating. There are many literatures available reported related to the surface modification of plasma sprayed coatings by post treatments like annealing and laser melting for molten salt applications for aerospace and gas turbine blades [116-118]; hence this review highlights the literature related to the post treatments for plasma sprayed coatings for pyrochemical reprocessing activity alone. Ravi shankar et al. [119] performed laser melting using a continuous wave CO\textsubscript{2} laser of 10.6 mm wavelength with a beam diameter of 1.5 mm to eliminate porosity and microcracks in the YSZ coating. The surface morphology of laser melted YSZ coating exhibited dense layer with segmented cracks on the surface. After laser melting the porosity decreased from 10% in the as-coated sample to 0.5% in the laser treated samples. Delamination occurred near the bond coat/ceramic interface in the coating as the thickness of the melted layer was high for higher laser power. With increasing laser power, the non-transformable tetragonal phase increased marginally in YSZ coating, which is beneficial for resisting to thermal shock [119]. Laser remelted surface exhibited a sharp interface with coarse and fine grains which was attributed to the reheating effect. The segmented crack on the surface of laser remelted sample decreased further by applying ZrO\textsubscript{2} and ZrO\textsubscript{2} + SiO\textsubscript{2} sealant and heat treating [120]. From the foregoing discussions, it is evident that post-plasma-spray treatments enhance surface properties and chemical bonding at the substrate/ceramic interface and the modified
microstructure would improve the physical, chemical and mechanical properties of the plasma-sprayed coatings. Based on the literature, post spray treatments were employed for the plasma sprayed ceramic coatings in the present work to enhance the properties of the coatings for molten salt applications in pyroreprocessing.

2.8 Need for the present study

The literature review suggests that the alloys and carbon materials employed for high temperature molten salt and uranium applications are prone to undergo degradation and attacked by molten salt and uranium medium; hence, providing ceramic coatings is the most appropriate method to protect the structural and container materials from molten salt as well as to control the reactivity with molten uranium. The corrosion studies reported in the literature were carried out on various materials in different molten salt systems, which are not relevant to the present application of carbon materials under molten LiCl-KCl salt medium to be used for the reprocessing of spent metallic fuels. Hence, this study assumes importance as there are not many reports on the corrosion behaviour of carbon materials in LiCl + KCl salt is available. The present work also attempts to emphasis the need for developing coatings on carbon materials for pyroreprocessing applications. The ceramic coatings identified were deposited on graphite for handling molten salt as well as melting of uranium. The developed ceramic coatings will be evaluated under demanding environments (molten salt, reactive metallic uranium at high temperatures) of the salt purification vessel and cathode processor crucible. The complete and in-depth microstructural analysis is carried out on carbon and coated materials by various characterization techniques to understand the mechanism of interactions and phase changes affecting the performance of the coated as well as uncoated carbon materials under the above environments.
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