CHAPTER 6

PLASMA SPRAYED PARTIALLY STABILIZED ZIRCONIA COATING ON HIGH DENSITY GRAPHITE

Corrosion studies were performed on plasma sprayed partially stabilized zirconia (PSZ) coated high density (HD) graphite with NiCrAlY bond coat in molten LiCl-KCl eutectic salt at 873 K for periods of 250, 1000 and 2000 h under argon atmosphere. There is no significant attack and degradation of top PSZ coating in molten salt, however microcracks were observed at the bond coat-substrate interface after 2000 h of exposure. PSZ coated HD graphite exhibited excellent corrosion resistance in molten LiCl-KCl salt due to chemical stability and stable phases as confirmed from SEM and XRD studies. Laser Raman spectra (LRS) analysis of corrosion tested PSZ coating showed only tetragonal phase of zirconia irrespective of exposure time due to the absence of phase transformation even after 2000 h of exposure. However, reduction in the intensity of tetragonal phase as increasing upon exposure time was found from LRS mapping of molten salt exposed PSZ coating. Molten uranium interaction studies were carried out on the PSZ coated HD graphite by melting uranium metal at 1623 K using induction heating system. Microstructural analysis of PSZ coating by SEM, XRD and LRS after uranium melting demonstrated that PSZ did not form any significant reaction layers and products with molten uranium. Thermal cycling studies carried out at 873 and 1023 K up to 200 cycles did not show any failure of the coating. Segmented cracks were generated after 100 and 200 cycles at both the temperatures.
6.1 Introduction

High density (HD) graphite is proposed and seleted as one of the candidate materials for various equipment in pyrochemical reprocessing plant (Chapter 1) for handling molten chloride salt as well as molten uranium at high temperature environment based on its corrosion behaviour as discussed in Chapter 4. Due to limited life of application as crucibles and liners, with the requirement of replacement and accumulation of solid waste, the use of HD graphite without coating becomes a critical issue as it will generate more solid waste. To avoid such circumstances, alumina-40wt% titania coating on HD graphite with and without bond coat attempted. The performance of alumina-40wt% titania coating was not up to the mark as discussed in Chapter 5. Hence it is necessary to select a ceramic coating meeting all requirements and perform well without significant change in structure and property during service. Yttria stabilized zirconia (YSZ) is one of the internationally proved ceramic coating for high temperature molten salt applications [1]. Based on the international experience YSZ coating was chosen for current application for molten LiCl-KCl salt as well as for molten uranium with temperatures ranging from 773-1573 K. Zirconia and Yttria has stability in highly corrosive environments like Cl₂, O₂ and UO₂Cl₂+Cl₂ [2]. Partially stabilized zirconia (PSZ) with 8 wt % Y₂O₃ coating exhibited excellent thermal stability and maximum thermal cycle life [3]. The plasma spray process is an economical method for producing reproducible and durable thick PSZ coatings for molten salt applications [4]. Oxides are usually coated on graphite substrates by thermal spray process as mentioned in Chapter 5. The adhesion between oxides and graphite can be increased with suitable bond coat applied between them [5]. In the present investigation surface protection of HD graphite with PSZ coating as top coat and
NiCrAlY as bond coat was chosen because of excellent stability and corrosion resistance to molten salts [6-9].

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are the most common techniques used for characterization of corrosion tested YSZ coatings in molten LiCl-KCl salt. Laser Raman spectroscopy (LRS) is also an effective tool for studying the corrosion behaviour of YSZ coatings exposed to molten salt with respect to phase composition and stability [10,11]. Hamilton et al. [10] performed in-situ Raman study to understand the attack of YSZ by Na$_2$V$_2$O$_6$ molten salt and leaching of yttrium from the YSZ. Raman imaging is a powerful technique used for representation of Raman spectra information in a visual form that can be more easily understood [12]. Mayoral et al. [11] proposed Raman mapping as one of the wrathful techniques to detect the variation in the composition as well phase changes of the YSZ coating. Micro-Raman imaging studies were performed by Bowden et al. [13] to understand the stress induced phase transformation in MgO-stabilized zirconia ceramics; it was revealed that phase transformation will occur after indentation with a higher content of monoclinic phase at the grain boundary. Raman imaging was adapted to visualize the variation of phases present in the Raman spectra. There are a number of reports in the literature concerning Raman imaging studies on PSZ material/coatings to understand the mechanical behaviour after indentation processes [13-15]. Up to now, no study has been reported on the Raman microscopy and imaging of PSZ coatings exposed to molten LiCl-KCl salt. Hence, it was attempted to utilize Raman imaging technique for mapping of corrosion tested PSZ coatings to understand its corrosion behavior in detail.

Various coating materials were evaluated in order to achieve a durable coating which facilitate the ingot release, minimize contamination and loss of uranium metal for processing.
of molten uranium. The application of these materials including YSZ coating for uranium consolidation in cathode processor operation was already discussed in the literature review (Chapter 2). The processing steps involved in the pyroreprocessing are batch process. Therefore it necessary to study the effect of temperature gradient on coated structural material to understand the coating performance under such demanding conditions [16]. The plasma-sprayed ZrO2-12 wt.% Y2O3 coatings subjected to thermal cycling at 1473 K with and without bond coats of Ni-Cr-Al-Zr in the atmosphere and the cracking behavior was correlated with acoustic emission technique data [17,18]. Joshi et al [19] studied extensively thermal cycling behaviour of YSZ coatings with the variation of following parameters: plasma arc current, spray distance, powder feed rate, coating thickness, bond coat material. Many groups/researchers performed thermal cycling studies in air environment reported that oxidation of bond coat occurred at high temperatures due to the formation of thermally grown oxide (TGO) during thermal exposure at high temperature for a long time and the TGO grew further as the thermal cycles increased. This TGO growth is believed to play a crucial role to the life of the coating and induced the strain energy for the crack propagation during the spallation. The life of a thermal spray coating during furnace cycling greatly depends upon its microstructure [19]. Hence, studying the microstructure of the PSZ coating has great importance to understand the initiation of cracks and failure phenomenon of the coating. To our knowledge, no literature concerning the thermal cycling of NiCrAlY bond coat and top PSZ coating on HD graphite is available. In order to ascertain the performance of the coatings, coated substrates were subjected to repeat heating and cooling cycles. The failure mechanisms of the TBCs are different from that of the analysis of the present investigation and it cannot be comparable to that extent due to variation in testing environments and
parameters. According to the specific requirement, the minimum number of thermal cycles required in order to pass the thermal cycling test is 200 cycles. Hence in the present thesis the thermal cycling test was carried up to 200 cycles.

The aim and objectives of this Chapter is to develop of PSZ coating on HD graphite and evaluation of coating performance under various conditions. This Chapter contains three sections related to the evaluation of PSZ coatings as: (1) Investigation of corrosion behaviuor in molten salt, (2) Compatibility with molten uranium and (3) Thermal cycling behavior up to 200 cycles.

6.2 Experimental

Different experiments were carried out to evaluate the performance of PSZ coatings in this Chapter (the detailed description about the testing and characterization techniques is provided in Chapter 3).

1. Deposition of PSZ coating on HD graphite by plasma spray process with NiCrAlY bond coat with optimized parameters and characterization with SEM-EDX, XRD and Raman spectroscopy techniques.

2. The corrosion studies were carried out on PSZ coated HD graphite in molten salt test assembly at 873 K for 500, 1000 and 2000 h by immersion in molten LiCl-KCl salt under ultra high pure (UHP) argon atmosphere. Corrosion tested PSZ coatings were characterization with visual examination, weight change and SEM-EDX, XRD and Raman spectroscopy techniques.

3. For in detailed understanding of corrosion performance of PSZ coating, Raman imaging studies were carried by Raman spectroscopy on all the exposed coatings.
4. Uranium metal melting experiments were carried out on PSZ coated HD graphite samples at 1623 K, after uranium melting the PSZ coatings were characterized with visual examination, SEM-EDX, XRD and Raman spectroscopy techniques.

5. The thermal cycling studies on PSZ coated HD graphite samples were conducted in an automated furnace at 873 and 1023 K under vacuum. Tested samples were characterized by weight loss, visual examination, SEM-EDX, XRD and Raman spectroscopy.

6.3 Results and Discussion

6.3.1 Corrosion behaviour in molten LiCl-KCl salt

6.3.1.1 Visual examination and weight change calculations

For comparing the corrosion behaviour of uncoated HD graphite with PSZ coated HD graphite, HD graphite samples were immersed in molten LiCl-KCl salt for 250, 1000 and 2000 h. Visual examination of uncoated HD graphite (Fig. 6.1a) clearly showed the two distinct regions of molten salt immersion and vapour exposed regions compared to as-received graphite. Severe attack was observed at immersion region compared to the vapour exposed region. The attack was uniform throughout the immersion region. In case of PSZ coatings (Fig.6.1b) it can be seen two different regions of immersion and vapour exposed regions as compared to as-coated HD graphite. No detachment or thinning of the coating was observed in the immersion as well as in vapour exposed regions.

The weight change of the HD graphite and its PSZ coated specimens after the corrosion test in molten LiCl-KCl salt for various durations under UHP argon atmosphere was measured. The percentage weight loss of uncoated HD graphite for 250, 1000 and 2000 h were 0.033, 0.126 and 0.235 respectively. These results indicated that the weight loss (%)
increased linearly with increasing time of exposure. The PSZ coated HD graphite showed insignificant weight gain due to the presence of salt deposits over the surface. It can be inferred from the weight loss measurements that uncoated HD graphite suffered more corrosion attack, when compared to PSZ coated specimens. The weight change measurements revealed that PSZ coating perform very well in molten LiCl-KCl salt at 873K.

![Visual examination of uncoated and PSZ coated HD graphite rod samples](image)

Fig. 6.1 Visual examination of (a) uncoated and (b) PSZ coated HD graphite rod samples before and after corrosion test in molten LiCl-KCl for 2000 h.

6.3.1.2 Surface morphology of immersion tested uncoated HD graphite

SEM micrographs of HD graphite under unexposed and exposed conditions are shown in Fig. 6.2. The increase of molten salt attack with time on HD graphite can be clearly seen from the SEM micrographs. The unexposed HD graphite surface contained pores and microcracks as shown in Fig. 6.2a. The surface morphology of 250 h exposed specimen showed lesser attack and initiation of graphite degradation was clearly seen in the micrograph (Fig. 6.2b) but the attack was significant in the case of 1000 h exposed (Fig. 6.2c) and was severe in 2000 h exposed specimens. The mechanism involved in the molten salt corrosion of
graphite was explained in Chapter 4, section 4.3.6. In the SEM image of 2000 h exposed sample (Fig. 6.2d) rough surface morphology was observed when compared to unexposed graphite. The graphite particles get dislodged from the surface into the molten salt as the salt have penetrated through the surface pores of the HD graphite [20].

![Fig. 6.2 SEM micrographs of as received and corrosion tested HD graphite in molten LiCl-KCl salt at 873 K (a) as received, (b) 250 h, (c) 1000 h and (d) 2000 h.](image)

Hence, it can be inferred from the weight loss measurements and surface morphology results that graphite undergoes substantial attack in molten salt. Therefore with increase in time of exposure the carbon particles in graphite start to degrade, which caused material loss, grooves and cavities on the surface as shown in Fig. 6.2b-d. Throughout the exposed region uniform attack was found on the surface of HD graphite. The pores present in the unexposed graphite surface were more widened after corrosion test. Several oxidants and impurities present in the
molten salts are responsible for accelerating the degradation of HD graphite in LiCl-KCl salt. Comparing the SEM micrographs of HD graphite, it was clear that porosity present in the unexposed graphite increased the weight loss with time of exposure to molten salt. The corrosion behaviour of HD graphite in molten salt suggested that protective coating was essential to avoid degradation in molten salt.

6.3.1.3 Surface morphology of immersion tested PSZ coated HD graphite

The surface morphology of as-sprayed coating (Fig. 6.3a) exhibits typical splat morphology with pores, inter splat voids and microcracks. Figures 6.3b, c and d shows the surface morphology of PSZ coated HD graphite exposed to molten LiCl-KCl salt at 873 K for 250, 1000 and 2000 h respectively. Surface morphology of corrosion tested PSZ coating exposed for 2000 h in molten salt was similar to that of as-sprayed morphology. All the exposed samples exhibited the formation of dense outer layer and deposition of salt over the surface. It was observed that there was insignificant surface changes after corrosion testing in molten salt for 2000 h exposed coating (Fig. 6.3d). Comparing the surface morphology of corrosion tested YSZ coated on metallic substrate [6,7], it was clear that there was no significant degradation or changes in the surface morphology of YSZ top coat in both the cases. In general, the presence of impurities like moisture, water and oxygen present in the molten salts will accelerate the corrosion process by dissolution and leaching of the elements. Uniform corrosion, dissolution and leaching are the common form of molten salt corrosion among that selective leaching is very common form at high temperatures [21]. To identify the elemental composition of the coating; EDX spectra was collected on the 2000 h exposed top PSZ coatings as shown in Fig. 6.4. Although the intensity of Y peak was less, significant amount of yttrium was shown in the elemental composition. EDX spectrum of 2000 h
exposed the coating (Fig. 6.4) showed Zr (61.89 wt%), O (28.32 wt%) and Y (9.78 wt%) elements similar to the as-sprayed coating. The presence of yttrium in the EDX analysis clearly indicated that no selective leaching and dissolution of yttrium occurred from coating into molten salt. This indicates that the absence of depletion of Y$_2$O$_3$ from PSZ in molten LiCl-KCl salt at 873 K.

![Surface morphology of (a) as-sprayed and immersion tested PSZ coatings in molten LiCl–KCl salt at 873 K for (b) 250 h, (c) 1000 h and (d) 2000 h.](image)

**Fig. 6.3** Surface morphology of (a) as-sprayed and immersion tested PSZ coatings in molten LiCl–KCl salt at 873 K for (b) 250 h, (c) 1000 h and (d) 2000 h.

![EDX spectrum of PSZ coating after exposed to molten LiCl-KCl salt for 2000 h.](image)

**Fig. 6.4** EDX spectrum of PSZ coating after exposed to molten LiCl-KCl salt for 2000 h.
The possible reaction of ceramics with oxygen and chlorine containing salt was proposed by Haanappel et al. [22] as shown below:

$$MO(s) + Cl_2(g) \rightarrow MCl_2(g) + \frac{1}{2}O_2(g) \rightarrow MO(s) + Cl_2(g) \text{ (Where M= Zr, Y)} \quad \ldots \ldots \ldots (1)$$

Oxides have better stability in chlorine environments and the standard Gibb’s free energy change for the reaction of ZrO$_2$, Y$_2$O$_3$ with chlorine at 873 K is shown below [2]:

$$\frac{1}{2}ZrO_2 + Cl_2(g) \rightarrow ZrCl_4(g) + \frac{1}{2}O_2(g) \Delta G^\circ =79 \text{ kJ/mol} \quad \ldots \ldots \ldots (2)$$

$$\frac{1}{3}Y_2O_3 + Cl_2(g) \rightarrow \frac{2}{3}YCl_3(g) + \frac{1}{2}O_2(g) \Delta G^\circ=22 \text{ kJ/mol} \quad \ldots \ldots \ldots (3)$$

These reactions clearly indicated that the YSZ has good stability. Various defects like pores, voids in between the splats, microcracks and thermal stresses were generated in the PSZ coatings (Fig. 6.3a) due to rapid solidification and shrinkage of ceramic particles during plasma spraying. Initially these microcracks and porosity present in the as-sprayed coatings act as penetration path for the molten salts. It was repoted that, the dense oxide layer formed on the surface during exposure would prevent further penetration of salt into the coating [8,9]. Thus the attack and dissolution of coating in molten salt has been prevented by the formation of protective dense layer on all the exposed surfaces. The present study revealed that PSZ coating exhibited better corrosion resistance in molten LiCl-KCl salt and provided superior protection to HD graphite.

### 6.3.1.4 Cross sectional morphologies of immersion tested PSZ coated HD graphite

Figure 6.5a shows the cross section of as-sprayed NiCrAlY bond coat followed by PSZ top coat on HD graphite. Top PSZ and bond coats exhibited laminar morphology, which is characteristic microstructural feature of plasma sprayed coatings. The bond coat generally improved the adhesion strength and coating integrity between top ceramic coat and substrate material [8]. X-ray elemental maps of as-sprayed coating shown in Fig. 6.5b clearly indicated
that top coat mainly composed of ZrO$_2$ ($Y_2O_3$ stabilization) and the bond coat consisted of Ni, Cr, Al and Y. In order to understand the distribution of elements in the exposed coatings, EDX analysis was carried out on cross sections of 1000 and 2000 h samples.

![Cross sectional back scattered SEM images of as-sprayed PSZ coating on HD graphite and X-ray elemental mapping of Zr, Y, O, C, Ni, Cr and Al.](image)

**Fig. 6.5** (a) Cross sectional back scattered SEM images of as-sprayed PSZ coating on HD graphite and (b) X-ray elemental mapping of Zr, Y, O, C, Ni, Cr and Al.

The interfaces of PSZ/NiCrAlY and NiCrAlY/graphite were analysed by EDX line scans on 1000 (Fig. 6.6) and 2000 h (Fig. 6.7) exposed samples. The elements of Zr, O and Y were distributed in the top coating and, Ni, Cr, Al, Y were present in the bond coat even after the corrosion test for 1000 and 2000 h test in molten LiCl-KCl salt. But a variation in the distribution of elements in 2000 h exposed sample especially in the Cr and Al line profiles was observed (Fig. 6.7). Elements of metallic bond coat particularly Cr and Al were diffused into HD graphite substrate through pores on the substrate. Cross section SEM micrographs of
immersion tested PSZ coated HD graphite after 1000 and 2000 h exposure in molten LiCl-KCl salt are shown in Fig. 6.8. The top coat of PSZ showed few microcracks in 1000 (Fig. 6.8a) and 2000 h (Fig. 6.8b) exposed samples because of origin of stresses in the coating after exposure to molten salt [23]. Also in case of 2000 h exposed sample the bond coat was discontinuous along cross section and was merged with graphite substrate (Fig. 6.8b).

![Cross section of 1000 h exposed PSZ coated HD graphite with NiCrAlY bond coat and corresponding EDX line profiles of Zr, Y, O, Ni, Cr, Al and C elements.](image)

The cross section micrographs does not show any degradation and penetration of salt through the PSZ coating cross section. However microcracks were identified at the interface of NiCrAlY/graphite and not at the NiCrAlY/PSZ interface. Formation of cracks in the coating
was due to the development of stresses at the bond coat-graphite interface. The mismatch of thermal expansion coefficient between metallic bond coat and HD graphite lead to the development of such stresses at the interface [23]. But no spallation or peel off of coating was observed on HD graphite substrate even after 2000 h test in molten salt. Thus for further long term exposure to molten salt, PSZ coating on HD graphite with good bond coat is required to achieve good adhesion to the substrate.

Fig. 6.7 Cross section of 2000 h exposed PSZ coated HD graphite with NiCrAlY bond coat and corresponding EDX line profiles of Zr, Y, O, Ni, Cr, Al and C elements.
Fig. 6.8 Cross sections of corrosion tested PSZ coated HD graphite in molten LiCl–KCl salt at 873 K for (a) 1000 h and (b) 2000 h.

6.3.1.5 XRD studies on immersion tested PSZ coated HD graphite

XRD pattern of as-sprayed PSZ coating on HD graphite is shown in Fig. 6.9a. According to XRD results as-sprayed coatings consisted of tetragonal and cubic phases (Fig. 6.9a). In plasma sprayed PSZ coatings, zirconia transform to tetragonal modification ($t'$) phase in cubic fluorite matrix [24] due to rapid solidification of sprayed powders. This non transformable tetragonal phase has been responsible for excellent strength and crack toughness [3]. After molten salt corrosion, the XRD patterns of the surfaces of 250, 1000 and 2000 h samples are shown in Fig. 6.9b-d. No new phase corresponding to corrosion product was present in the coating after corrosion test for 2000 h indicating good chemical
compatibility of PSZ coatings in molten LiCl-KCl salt. Corrosion studies performed in sodium metavanadate molten salts have reported phase transformation from cubic/tetragonal to monoclinic after corrosion test due to leaching of yttrium from the ceramic coating [24]. But no such phase transformation from tetragonal to monoclinic due to absence of leaching of yttrium was observed from XRD after corrosion test in the present study as shown in Fig. 6.9a-d. This result was supported by EDX analysis on the exposed PSZ coatings for 250, 1000 and 2000 h. The absence of corrosion products and phase transformations, clearly showed that YSZ on HD graphite was stable in molten LiCl-KCl salt.

Fig. 6.9 XRD pattern of (a) as-sprayed, (b) 250 h, (c) 1000 h and (d) 2000 h corrosion tested PSZ coated HD graphite in LiCl-KCl salt.
6.3.1.6 Raman studies on immersion tested PSZ coated HD graphite

LRS is an effective tool for the characterization of YSZ coatings [10,11,25,26] to understand the attack of molten salt [10,24]. LRS is a useful tool to investigate the phase transformation in stabilized ZrO$_2$, because it determines the change in the bond length and the angle between the cation and anion [27]. Raman spectroscopy is one of the powerful techniques to identify phase changes in YSZ coatings exposed to highly aggressive environments [10]. Raman spectrum arises in YSZ mainly due to the polarizability associated with the oxygen ion vacancies produced by Y$_2$O$_3$ [28]. In the present investigation, LRS experiments were carried out on as-sprayed and corrosion tested PSZ coatings in molten LiCl-KCl salt at 873 K for 250, 1000 and 2000 h to identify the phase changes of PSZ coatings due to high sensitivity of Raman spectroscopy to these ceramics. The Raman spectra showed (Fig. 6.10) distinct peaks at 148, 250 and 638 cm$^{-1}$ due to the presence of dominant tetragonal ZrO$_2$ phase [10,11]. In addition to that, weak peaks were obtained at 333 and 471 cm$^{-1}$ which can be attributed to the tetragonal ZrO$_2$ phases. However, those peaks were shifted to a large wave number difference due to surface defects and heterogeneities. The designation of the modes according to Ref. [25] is as defined for PSZ with yttria system. Table 6.1 depicts the tentative assignments of the peaks seen in Raman spectra of as-sprayed and exposed PSZ coatings for 250, 1000 and 2000 h. One more observation was that all the Raman spectra were similar in terms of all spectral positions irrespective of the increase in exposure time to molten LiCl-KCl salt. Also, the peaks due to sp$^2$ carbon impurities were observed in all cases [29]. From Fig. 6.10, it was clear that Raman spectrum of as-sprayed coating was similar to that of corrosion tested samples and the phases present in the as-sprayed coating were still observed even after 2000 h at 873 K. The Raman spectra collected at different regions on corrosion
tested PSZ coating revealed same spectral features as observed in Fig. 6.10. All the spectra contained tetragonal phase along with carbon impurities (Table 6.1), and no variation or change in spectral positions were observed.

Fig. 6.10 Raman spectra of as-sprayed and corrosion tested PSZ coating over HD graphite for 250, 1000 and 2000 h in LiCl–KCl salt at 873 K.

The full width at half-maximum (FWHM) values of the Raman lines near 638 cm$^{-1}$ of the characteristic peak of the tetragonal phase were measured to compare the structural disorder of the tetragonal phase in the as-sprayed coating to molten salt tested 1000 and 2000 h coatings. The FWHM of the Raman lines near 638 cm$^{-1}$ in the as-sprayed coating is approximately 33.7 cm$^{-1}$; in the corrosion tested coatings were 33.8 and 34.9 cm$^{-1}$ for 1000 and 2000 h exposed coatings respectively. The broadening of Raman line width indicated an increasing structural disorder of the tetragonal phase in the molten salt exposed coating [30]. The increase in FWHM was quite low (1.2 cm$^{-1}$) from as-sprayed to 2000 h exposed coatings and hence, much pronounced disorder was not observed in the tetragonal phase after exposure to molten LiCl-KCl salt. Stresses can also develop with time as a result of mechanical/physical property changes in the coating after exposure to aggressive molten salts.
This microstructural feature was supported by a close observation of average Raman spectra of 2000 h exposed coating (Fig. 6.11) at 250 cm\(^{-1}\) which showed a shift in the peak position was due to the generation of stresses in the PSZ coating after exposure to molten salt.

**Table 6.1 Raman peak assignments of as-sprayed and immersion tested PSZ coated on HD graphite specimens in molten LiCl-KCl salt for 250, 1000 and 2000 h.**

<table>
<thead>
<tr>
<th>Band (cm(^{-1}))</th>
<th>Assignments</th>
<th>Symmetry</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>tetragonal</td>
<td>E(_g)</td>
<td>[25]</td>
</tr>
<tr>
<td>250</td>
<td>tetragonal</td>
<td>E(_g)</td>
<td>[25]</td>
</tr>
<tr>
<td>333</td>
<td>tetragonal</td>
<td>A(_g)</td>
<td>[25]</td>
</tr>
<tr>
<td>471</td>
<td>tetragonal</td>
<td>B(_g)</td>
<td>[25]</td>
</tr>
<tr>
<td>638</td>
<td>tetragonal</td>
<td>B(_g)</td>
<td>[25]</td>
</tr>
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From Raman analysis it was inferred that no phase transformation occurred even after exposure to corrosive molten LiCl-KCl salt environment, and that the top PSZ coatings exhibited excellent corrosion resistance towards molten LiCl-KCl salt.

![Fig. 6.11 Average Raman spectrum showing stresses distribution in PSZ coating exposed to molten LiCl-KCl salt for 2000 h.](image)
6.3.1.7 Raman imaging/mapping studies on immersion tested PSZ coated HD graphite

Raman mapping was carried out on PSZ coatings after exposure to molten LiCl-KCl salt for 250, 1000 and 2000 h in order to understand in-depth the reason for disorder, microstructural and any phase change/variation information. The light microscopy images as shown in Fig. 6.12a, b and c represent the area of interest from which the average Raman spectra was collected. In Fig. 6.12 all three exposure time periods of PSZ coatings revealed tetragonal phase of zirconia only in the average Raman spectra. Single Raman spectra data was strongly supported by average Raman spectra. Generally, Raman map gives the intensity distributions of one particular spectral range from which the changes in the composition of a specific component can be determined. In the present study we selected 36 number of data points and hence the image obtained was coarse. Raman map represented the image distribution of one particular wave number range where as the light microscopic image depicts the distribution of all the components [31].

Fig. 6.12 Average Raman spectra and selected light microscopy area images of PSZ coatings after exposed to molten LiCl-KCl salt at 873 K for (a) 250, (b) 1000 and (c) 2000 h.
Raman maps were recorded from 131-167 cm\(^{-1}\) with a central peak position 150 cm\(^{-1}\) corresponds to tetragonal phase of zirconia [11]. The results of tetragonal Raman map at 150 cm\(^{-1}\) showed in Fig. 6.13b represents the change in the tetragonal phase with increasing the time of exposure to molten LiCl-KCl salt. As the exposure time increases molten LiCl-KCl salt created cracks, voids and pores in the PSZ coatings, and these features were indicated as white colour in the mapping images. The exposed PSZ coatings exhibited significant decrease in the intensity of tetragonal phase with increase in exposure time. The reduction in intensity is due to increase in microstructural inhomogeneities like cracks (Fig. 6.13a), voids, pores etc. Similar results have been recorded for Raman maps from 600-675cm\(^{-1}\) with a central peak position 638 cm\(^{-1}\) corresponding to tetragonal phase of zirconia as shown in Fig. 6.13c. The most important finding from Raman mapping was that average Raman spectra (Fig. 6.12) showed no phase other than tetragonal, however there was a change in the Raman imaging intensity of tetragonal phase from 250 to 2000 h (Figs. 6.13b and c). The molten LiCl-KCl salt exposure did create voids and cracks but did not favour leaching of yttrium leading to the formation of monoclinic phase. The decrease of tetragonal phase intensity in the Raman mapping was mainly due to the increase in the microstructural inhomogeneities as the exposure time increased from 250, 1000 and 2000 h as observed in SEM cross section images in Fig. 6.13a. These are represented as white colour region in the mapping results (Figs. 6.13b and c). Raman analysis in the present investigation was supported by XRD studies performed on YSZ coatings exposed to LiCl based molten salt at 600°C and their results revealed tetragonal phase only before and after corrosion test for different time period of exposure [8,9].
Fig. 6.13 (a) SEM micrographs on cross-section of exposed PSZ coating and Raman intensity mapping images corresponding to the (b) central peak position at 150 cm$^{-1}$ and (c) at 638 cm$^{-1}$ of PSZ coating tested in molten LiCl-KCl salt at 873 K for 250, 1000 and 2000 h. In Raman image, the coloured regions indicate the intensity of tetragonal phase and the white colour regions indicates the micro-cracks, voids and pores created regions and also carbon impurity.
6.3.2 Uranium melting

6.3.2.1 Compatibility studies based on Gibbs free energy and visual examination

Towards the chemical reactivity of molten uranium with the coating materials, the Gibbs free energy change ($\Delta G_R$) was calculated using Factsage® version 6 software for the following reactions in the temperature range 300 - 2000 K.

\[
\begin{align*}
\text{ZrO}_2 + U & \rightarrow \text{UO}_2 + \text{Zr} \\
\text{Y}_2\text{O}_3 + 1.5 \text{ U} & \rightarrow 1.5 \text{ UO}_2 + 2\text{Y}
\end{align*}
\]

Evaluating ($\Delta G_R$) values computed for the reactions (4) and (5) are plotted as a function of temperature in Fig. 6.14. The thermodynamic stability of the PSZ coating with respect to molten uranium can be ascertained from the values of Gibbs free energy change for the formation of all probable binary compounds from the constituents of coating materials and molten uranium in the temperature range of investigation. Figure 6.14 shows that the reaction between ZrO\textsubscript{2} and U is not feasible in the temperature range 300 to 2000 K as the value of Gibbs free energy change for reaction (4) is positive. The Gibbs free energy change for the reaction of Y\textsubscript{2}O\textsubscript{3} with uranium is more positive than the values for the reaction (4). In the temperature range of 300 - 2000 K, the Gibbs free energy change for these reactions (4) and (5) are positive and hence, the stability domain of YSZ showed lie within the $\Delta G_R$ - T plots between ZrO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3} in Fig. 2, revealing that uranium will not react with YSZ. This fact is corroborated by the results reported in the literature that ZrO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3} are chemically inert against the attack by uranium [32-34]. Thus, it is expected that coating of YSZ on graphite crucibles would eliminate the problem of interaction of molten U with the graphite container [32].
Figure 6.15 shows the pictures of PSZ coating on HD graphite before and after uranium melting experiments. Visual examination as-sprayed PSZ coating showed the change in colour from white to black after uranium melting. The region where uranium was melted could be identified on coating surface.

Fig. 6.14 Gibbs free energy change of possible chemical reactions as a function of temperature.

6.3.2.2 Morphology of uranium melted PSZ coatings

Figure 6.16a shows the surface features of a typical plasma sprayed PSZ coating. The splat morphology continued to be present in the PSZ coating after single uranium melting (Fig. 6.16b). After the second time uranium melting no reactive layer of uranium was formed on PSZ coated surface (Fig. 6.16c) due to the absence of reaction between U and PSZ. However, microcracks were generated on the surface of PSZ coating (Fig. 6.16d) due to rapid heating of PSZ coating and cooling to room temperature. Stresses can be generated in the microstructure (Fig. 6.16a) owing to the contraction of individual splats formed during rapid cooling ($10^6$-$10^8$ K/s) and resolidification on the colder substrate; or on a layer of previously
solidified splats and these are called as ‘quenching stresses’ [35,36]. These stresses have strong influence on the microstructure and performance of coatings. Stresses were relaxed by forming microcracks in the coating due to the high heating rate of 90°C/min.

Fig. 6.16 Surface morphology of PSZ coating: (a) as-sprayed (BSEI), (b) single run and (c and d) double run uranium melted coatings.

Elemental analysis carried out by EDX (Fig. 6.17a) on selected regions of uranium melted coating (Fig. 6.17b) showed the presence of only coating elements Zr (67.41 wt %), Y (09.71 wt %) and O (22.88 wt %). Elemental peak of U was not identified on the tested coatings and the uranium (00.00 wt %) concentration is below the detection limits.
Fig. 6.17 (a) EDX spectrum of second time uranium melted PSZ coating surface of (b) selected area and corresponding EDX elemental mapping of Zr, Y and O and (c) line scan on the surface.
The evidence of absence of reaction between molten uranium and PSZ was further confirmed by X-ray elemental maps and lines scans on the surface of two times uranium melted coating. The elemental mapping of Zr, Y and O clearly showed the distribution of coating elements on the surface of PSZ coating after uranium melting. Black regions in the mapping images are unfocused regions due to surface irregularities and hence, no element was identified.

Figure 6.17c shows the line scans for different elements of coating along the top PSZ surface which clearly demonstrated that the uranium concentration was below the detection limits. The change in the signal intensity was possibly due to surface roughness. Even though uranium melting was performed with high heating rate no significant detachment of PSZ coating was observed from HD graphite after uranium melting experiments as could be seen in Figs. 6.18 and 6.19. Cross sectional micrograph of single time uranium melted PSZ coating in the secondary electron image (SEI) exhibited similar morphological features of as-sprayed coating like laminar morphology and pores on the top PSZ coating. Microcracks were not observed at the interfaces (Figs. 6.18b and 6.19) of PSZ/NiCrAlY and NiCrAlY/graphite after testing. But microcracks were observed within the ceramic coating due to relieved tensile stresses usually formed in the YSZ coating during the operation at high temperature. Extensive analysis was carried out along the cross-section of PSZ coated HD graphite to identify any diffusion or penetration of molten uranium and also morphological variations across the thickness of the coating and the results are presented in Figs. 6.18b, 6.19 and 6.20. X-ray elemental mapping (Figs. 6.18b and 6.19) was obtained on the cross section of SEI to find out variations in elemental composition after single uranium melting. It is evident from the results that the Ni, Cr, Al and Y were still present in the bond coat region and top coat comprised the elements Zr, Y and O. Line profiles and elemental mapping showed low
intensity for Al and Y bond coat elements due to the low weight percentage of these two elements in the initial spray powder. From the line scan (Fig. 6.20) along the cross section of second time melted coating uranium concentration was found negligible in the PSZ coating on HD graphite (below the detection limits). This analysis was supported the EDX elemental mapping (Fig. 6.17b) and line scan (Fig. 6.17c) of the surface of PSZ after uranium melting. It was observed from the cross section micrographs of uranium melted PSZ coatings (Figs. 6.18, 6.19 and 6.20) that uranium has not penetrated through the pores on the surface. It was reported that penetration of liquid uranium into these pores was dependent on the surface tension and the contact angle [33]. Absence of reaction between uranium and PSZ in the EDX elemental mapping of uranium melted surface and cross section validated the discussion on the compatibility of U with PSZ based on Gibb’s free energy change as discussed in Section 6.3.2.1. Based on the results obtained in the presented work plasma sprayed PSZ is found compatible with molten uranium at 1623 K.
Fig. 6.18 (a) Cross sectional morphology (SEI) and (b) elemental X-ray mapping of the interface of PSZ/NiCrAlY/graphite after single time uranium melted on PSZ coating.
Fig. 6.19 Cross sectional morphology (SEI) and elemental X-ray mapping of the cross-section of PSZ coated HD graphite with NiCrAlY bond coating after second time uranium melting.
Fig. 6.20 Line scans of the cross-section of PSZ/NiCrAlY/graphite interface after second time uranium melting.

6.3.2.3 Phase analysis of uranium melted PSZ coatings

Figure 6.21a shows the XRD pattern of PSZ coating before and after uranium melting. Uranium melted PSZ coatings exhibited same crystallographic phases of as-sprayed coating. The existence of t'-form of tetragonal phase is too difficult to distinguish from the cubic phase by XRD analysis [37]. As per the phase diagram information on ZrO$_2$-Y$_2$O$_3$ system, in the temperature (1623 K) of interest in the present investigation of uranium melting the co-existence of non-transformable tetragonal (t') and cubic phases in the plasma sprayed 8 wt% yttria doped zirconia was evident [38]. The predominance of the t' phase in the coatings would be highly beneficial because of its high temperature stability and strength. The absence
of any reaction product on the surface of PSZ coating after second uranium melting was confirmed by XRD analysis. It was reported that YSZ coatings were stable up to maximum temperature 1573 K in normal atmosphere. In the present study the melting was carried out in UHP argon atmosphere. Hence, there was no interaction of molten uranium with oxygen to form any compounds and inducing any phase change in the coating.

Raman spectra (Fig. 6.21b) of as-coated and uranium melted PSZ coatings showed tetragonal phase peaks only and these were designated according to the modes assigned in the literature [25]. The designation of peaks in the Raman spectra of PSZ coatings are listed in Table 1. In the tetragonal phase of zirconia each Zr atom is surrounded by eight oxygen atoms, four of which form an elongated tetrahedron and the remaining four a flattened tetrahedron. Upon exposure to high temperatures or molten salts or any aggressive media, there is a possibility of change in the Zr–O bond length and bond angle in PSZ and this brings out a change in the Raman active mode [28]. Unlike the XRD analysis of the phases in the PSZ, Raman spectroscopy showed only peaks corresponding to tetragonal phase because tetragonal phase modes are more active than the cubic phase in the chosen composition of PSZ (i.e. Y₂O₃ 8 wt % in ZrO₂). The nature of the peaks and their position were found similar for as-coated and tested PSZ coatings. All the characteristic peaks of as-coated PSZ were also found to be present in the spectrum of uranium melted PSZ coating, though the peaks were marginally shifted by a few wave numbers and were more or less sharp as compared to that of the as-coated PSZ. This is due to generation and relaxation of stresses in the uranium melted PSZ coating during testing. This observation is in conformity with the SEM analysis (Fig. 6.16d) of uranium melted PSZ coating. Phase identification by XRD and Raman analysis on
uranium melted PSZ coatings confirmed that the PSZ coating was intact without any phase change or formation of any corrosion/reaction product.

![XRD and Raman spectra](image)

**Fig. 6.21** (a) XRD pattern and (b) Raman spectra of as-sprayed and uranium melted PSZ coatings.

### 6.3.3 Thermal cycling studies

#### 6.3.3.1 Porosity and visual examination

Plasma-sprayed coatings usually contain up to 10% porosity. Optical micrograph of cross-section of PSZ coated HD graphite is shown in Fig. 6.22. The microstructure clearly distinguishes the laminar morphology of bond coat, top coat regions and top coat contained some level of porosity. Area percentage porosity measured by according to the ASTM E 2109-procedure A [39] indicated that the porosity of the top PSZ coating is around 10%. Porosity was an important parameter which determines various properties of coatings like thermal shock and thermal cycling resistance [40].
After thermal cycling the PSZ coating samples were visually examined to identify the surface changes and coating spallation and to identify the crack initiation and failure of the coating. Table 2 shows a photograph of PSZ coated HD graphite samples after thermal cycling for 50, 100 and 200 cycles at 873 and 1023 K. The visual examination of thermal cycled PSZ coating after 50 cycles at 873 and 1023 K coating turns to light dark colour, after 100 cycles the coating color changed to black color at both the temperatures. However, at 1023 K coating was blacker than the 873 K tested PSZ coating. It is well known that degassing occurs in graphite at high temperatures in very low P$_{O_2}$ (vacuum) environment. As thermal cycling studies were performed in static vacuum, vapour of graphite would have deposited over YSZ coating and darkened its colour. It is also reported in literature that the colour of YSZ changes owing to loss of oxygen in YSZ in low oxygen and high temperature environments. Partially stabilized zirconia (PSZ) powder was used for top YSZ coating. In PSZ, the tetragonal phase of ZrO$_2$ is stabilized by the addition of 7-8 Y$_2$O$_3$ (by weight). As oxide ion vacancies already exist in PSZ, loss of very low quantity of oxygen is not expected.
to bring any deleterious effect. Nevertheless, YSZ coated graphite will be employed for
applications in ultra high pure argon atmosphere and the problem of oxygen loss will not
arise. Visually no macrocracking was observed on any of the PSZ coating surfaces tested up
to 200 cycles.

Table 6.2 Visual examination of thermal cycled PSZ coated HD graphite at 873 and 1023
K for 50, 100 and 200 cycles.

<table>
<thead>
<tr>
<th>Cycles ↓</th>
<th>Temperature</th>
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<tbody>
<tr>
<td></td>
<td>873 K</td>
<td>1023 K</td>
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<tr>
<td>50 cycles</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
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<tr>
<td>100 cycles</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
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<tr>
<td>200 cycles</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
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6.3.3.2 Weight loss studies thermal cycled PSZ coating

The percentage of weight loss of PSZ coating plotted as a function of thermal cycles is shown in Fig. 6.23. The weight loss was calculated after 50, 100 and 200 cycles at two different temperatures of 873 and 1023 K. From Fig. 6.23 it was clear that as the number of cycles increased the weight loss of the coating was increased at both the temperatures. The weight loss observed owing to the loss of coating material during thermal cycling; however, the weight loss was not due to the failure of the coating.

![Fig. 6.23 Weight loss (%) of thermal cycled PSZ coated HD graphite.](image)

6.3.3.3 Morphology of thermal cycled PSZ coatings

The as-sprayed PSZ coating surface morphology consists of splats, microcracks, voids between splats, unmelted oxides etc. (Fig. 6.24a). The morphology of the as-sprayed coating contain splat structures and splat is the ‘brick’ for the buildup of the deposit of coating [41]. These micro defects are common in plasma sprayed coatings due to the characteristics of process of deposition and they play significant role in determining the life or durability of the coatings when subjected to thermal cycling or thermal fatigue. According to Berndt et al. [17]
the failure mechanisms of plasma-sprayed TBCs are a complex function of
imperfections contained within the oxide coating and at the interfacial region and the
means by which these imperfections respond to thermal cycling. All failure mechanisms
of the thermal cycled coatings are affected by the microstructures of the coating [42].

Fig. 6.24 Surface morphologies of PSZ coating: (a) BSEI of as-sprayed and after 50
cycles (b) at 873 and (c) 1023 K.
The variations in the microstructure lead to the spallation or detachment of the coating from the substrate. Hence, the microstructure of the thermal cycled PSZ coatings were studied in detail with possible characterization techniques.

The surface morphologies of thermal cycled PSZ coatings after 50, 100 and 200 cycles at 873 and 1023 K is shown in Figs. 6.24, 6.25 and 6.26 respectively. After 50 thermal cycles at 873 and 1023 K the surface morphology of PSZ coating did not show marked effect and microcracks were present between the splats and on the splats present as in the as-sprayed coating. There is no enlargement or propagation of crack or breaking of splats which are not observed in PSZ coatings after 50 cycles at 873 (Fig. 6.24a) and 1023 K (Fig. 6.24b). At a certain stress levels, cracks form between the already sprayed layers and freshly sprayed lamella (inter lamellar cracks) [42]. After 100 and 200 cycles crack propagation was clearly observed in the SEM study.

Fig. 6.25 Surface morphologies of PSZ coating after 100 cycles at (a) 873 and (b) 1023 K.
The microstructure of the PSZ coating after 100 cycles at 873 K (Fig. 6.25a) exhibited network of cracks generated on the surface which significantly propagated throughout the coating for samples tested at 1023 K (Fig. 6.25b). The surface morphology examined in SEM after thermal cycled for 200 cycles (Fig. 6.26) also exhibited segmented network of cracks in both the PSZ coatings tested at 873 and 1023 K. As compared to 873 K tested PSZ coatings, 1023 K tested coating showed deep cracking as observed at higher magnification in Figs. 6.25 and 6.26. Three different types of cracks can be observed in the plasma sprayed coatings subjected to thermal cycling and these can be defined as follows: (1) segmentation cracks (cracks running perpendicular to the coating surface and penetrating at least half the coating thickness); (2) branching cracks (cracks with the direction parallel to the coating plane, starting from segmentation cracks); (3) delamination cracks (oriented horizontal cracks occurring between individual splats or lamellae) [43].

Fig. 6.26 Surface morphologies of PSZ coating after 200 cycles at (a) 873 and (b) 1023 K.
In case of 50 cycles tested PSZ coatings (Fig. 6.24) cracks are similar to the sprayed coating, but in case of 100 (Fig. 6.25) and 200 cycles (Fig. 6.26) tested PSZ coatings vertical cracks are observed in the thermal cycled PSZ coatings due to microcracking of splats during cooling. Two kinds of cracks observed in the 100 and 200 thermal cycled PSZ coatings are segmented cracks and branching cracks. Horizontal microrcaking lead to reduce thermal shock life [42,44] and these kind of delamination cracks are not observed in thermal cycled PSZ coatings up to 200 cycles. Once a single crack gets started, the crack encounters the stress fields associated with the geometrical arrays of cavities at most grain boundaries on the splats. Rapid crack link up takes place and macrocrack propagation occurs. The observed cracks on the surface of the coatings in SEM micrographs are microrcaks only and there was no macrocrack was observed visually on the PSZ coatings (Table 2). It was reported that catastrophic failure occurs at some stage when there was a transformation from the microcrack to a macrocrack network [18]. The interesting observation found in the present investigation was that with increase in thermal cycles the number of crack events were found increased in the coatings. Cracking and crack growth have been observed only in 100 and 200 cycles tested coatings.

Typical microstructures of as-deposited PSZ top coat with NiCrAlY bond coat by APS is shown in the backscattered electron image (BSEI) in Fig. 6.5. Porosity in the YSZ coating is considered advantageous for enhancing the coating life during thermal cycles [19]. The interlamellar porosity, resulting from poor adhesion between the splats, was evident. Porosity present in the coating and vertical microcracks generated during thermal cycling of the coatings gives the strain tolerance by lowering Young’s modulus of the coating [42,45]. Because of these features the coating will contain low stress values by stress relaxation
process, without that features, the ceramic coating system would hardly able to withstand the stress levels arising during thermal cycling [42]. The primary failure modes observed in TBC systems subjected to the thermal cycling in oxidizing environment are: (i) cracking of the bond-coat/TGO at the interface; (ii) cracking within the top-coat; and (iii) linking of these microcracks by fracture of the TGO [46]. In the present study the crack was initiated in the top PSZ coating and was propagated within the coating perpendicular to the substrate and propagated to cracking of bond coat as shown in Fig. 6.27b. To identify the elemental composition variation X-ray elemental mapping (Fig. 6.27) was carried out. No variation in the elemental distribution was noticed and no thermally grown oxide at the bond coat region was observed. The change in the co-efficient of thermal expansion with temperature between substrate, bond coat and top ceramic coat also generate stresses near the interface during the thermal cycling studies. Due to thermal stresses generated by the temperature gradients, possibility exists to generate interface cracking. However, from cross-sectional microstructure (Fig. 6.27 and 6.28) analysis of PSZ coating thermal cycled for 200 cycles at 873 and 1023 K did not exhibit any microcracks at the HD graphite/NiCrAlY and NiCrAlY/PSZ interfaces. Crack was observed only in top coating due to the cracking of splats and it propagated through splats by breaking them. This indicated that up to 200 cycles at 873 and 1023 K the coating showed good adhesion to graphite substrate.
Fig. 6.27 (a) Cross-sectional SEM micrograph and X-ray elemental mapping, (b) generated crack and (c) line scan along the coating thickness of PSZ coating after 200 cycles at 873 K.

The PSZ coating contains two kinds of stresses: (i) compressive stress at ambient temperature when the coated substrate is heated during thermal cycling. (ii) At high temperature the compressive stresses become tensile stresses in the YSZ coating [47] and these stresses relieved by forming cracks in the coating (Fig. 6.27 and 6.28). The changes
observed in the coatings are due to thermally induced changes only and there was no change in elemental composition was noticed. According to the literature, failure mechanisms of the thermal barrier PSZ coatings are closely associated with the oxidation of bond coat. In this study oxidation of the bond coat was not observed in elemental mapping or line scans carried out on tested PSZ coatings, because thermal cycling was carried out in vacuum to simulate the pyroprocessing plant conditions.

The generations of segmented cracks during thermal cycling studies will help to improve the life of coating by strain tolerance of the coating and increase the compliance of the coating. Many studies \cite{43,48} reported that segmented crack densities generated in TBCs before or during the thermal cycling test improve in the thermal shock or thermal cycle resistance compared to the TBCs with low segmentation crack density or without segmentation cracks. The controlled porosity, internal microcracking and segmentation have been observed in the thermal cycled PSZ coatings gave enough strength to coating; to exhibit good resistance to thermal cycling up to 200 cycles and coating spallation was not observed at both the temperatures. YSZ coating did not spall-off due to the plastic flow and creep at high temperatures of metallic bond coat of NiCrAlY facilitate to relieve the thermal stresses significantly.
Fig. 6.28 (a) Cross-sectional SEM micrograph and X-ray elemental mapping, (b) generated crack and (c) line scan along the coating thickness of PSZ coating after 200 cycles at 1023 K.

6.3.3.4 Phase analysis of thermal cycled PSZ coatings

The diffraction patterns of thermal cycled PSZ coating at 873 and 1023 K for 50, 100 and 200 cycles are shown in Fig. 6.29a, b and c. All the thermal cycled PSZ coatings mostly consist of a nontransformable tetragonal (t') phase along with cubic phase similar to the as-sprayed coating (Fig. 6.9a). In all three cases (50, 100 and 200 cycles) at two different
temperatures it was observed that there was no phase change. It was pointed out from the diffraction patterns that difficult to resolve accurately the overlapping cubic and tetragonal phases in the XRD patterns because these are very similar and they are differentiated by the characteristic peak splitting of the tetragonal phases [3,49]. Monoclinic phase was not detected in any of the tested coatings for 50, 100 and 200 thermal cycles. The t′ phase present in the thermal cycled PSZ coating will be highly beneficial because it gives excellent strength and crack toughness to the coating [3]. This is also one of the reasons for the coating having good thermal cycling resistance up to 200 cycles at 873 and 1023 K.

Fig. 6.29 XRD patterns of thermal cycles PSZ coatings at 873 and 1023 K after (a) 50, (b) 100 and (c) 200 cycles.
Raman spectra recorded from the surfaces of thermal cycled PSZ coatings after 200 cycles at 873 and 1023 K are shown in Fig. 6.30. Five bands observed in Raman spectra of all PSZ coatings and these five bands position (Table 1) confirms the presence of tetragonal zirconia present in the thermal cycled PSZ coatings similar to as-sprayed coating [50]. The peaks assignment was already discussed in Section 6.3.1.6. However, a minor shift in the peak position was observed due to the stresses in the thermal cycled PSZ coating. The segmented cracks formed in the coating observed in SEM indicated that stresses play a significant role in the thermal cycled samples. Due to these stresses Raman peaks were shifted from actual position to few wave numbers. This observation was in concurrence with the SEM analysis of the PSZ coating after thermal cycling. The temperatures of thermal cycling was carried are 873 and 1023 K. These temperatures are quite low for expecting phase change in YSZ system according to the phase diagram. Hence, the thermal cycling at these two temperatures not showed much marked effect on the stability of PSZ coatings up to 200 cycles. In general, the t’ phase transforms to the stable tetragonal phase (t) with low yttria content during the high temperature testing and subsequently to the monoclinic phase (m) during cooling to room temperature. The phase transformation of t to m is associated with a volume expansion of up to 5%. The volume expansion will deteriorate the integrity of PSZ topcoat and could hence cause the failure of coatings. Nevertheless, decomposition of t’ phase did not occur during thermal cycling studies. In the present investigation no phase transformation was observed up to 200 cycles at 873 and 1023 K in the XRD and Raman analysis. Therefore, it can be concluded that the absence of phase changes as evidenced in the present study did not cause any damage to the integrity of the PSZ coating system up to 200 cycles.
6.4 Summary

PSZ coatings were plasma sprayed on HD graphite with optimized process parameters and immersion tested in molten LiCl-KCl salt up to 2000 h under UHP argon atmosphere. PSZ coatings exhibited good corrosion resistance to molten LiCl-KCl salt even after 2000 h of exposure without spallation of coating and absence of phase transformation as evidenced in SEM-EDX and XRD analysis. Raman mapping of corrosion tested PSZ coatings for 250, 1000 and 2000 h results showed that as the exposure time increases the tetragonal phase intensity was decreased due to microstructural inhomogenities occurred in the coating after exposure. Molten uranium compatibility test with PSZ coatings at 1623 K proved that PSZ coating offer better stability and protection to HD graphite. Thermal cycling studies on PSZ
coating at 873 and 1023 K up to 200 cycles did not show any failure of the coating and exhibited segmented cracks throughout the coating. Based on the results PSZ coating on HD graphite performed well in molten salt and uranium melting and no significant changes to the integrity of coating was observed. Hence, it can be considered as a best choice coating for these applications and can be evaluated further with large scale experiments.

References


