CHAPTER V
CORROSION AND COMPATIBILITY STUDIES OF PLASMA SPRAY COATED LANTHANUM PHOSPHATE AGAINST MOLTEN URANIUM

5.1 Introduction

Critical parts in many manufacturing applications need to survive hostile environments imposed by high operating temperature and corrosive conditions. The normal engineering practice is to apply a protective coating of a ceramic material over such components and enhance their life time. Suitable alloy or ceramic material, which can withstand the corrosion, is applied on the substrate as a thin coating. The base material that provides the necessary mechanical strength and the protective surface coating prevents corrosive degradation. The coating–substrate composite is specific to the intended application.

Corrosion of melting pots and casting crucibles by molten uranium and its alloys is a major problem in the nuclear industry. Ceramic coatings can be given on graphite, tantalum and molybdenum crucibles that are used for melting and high temperature processing of uranium and its alloys. The protective ceramic coating should not react with the material of the crucible and also it should be chemically inert to liquid/vapour uranium. As discussed previously, LaPO₄ (monazite) has high melting point, thermal stability and does not react with uranium liquid and vapour. Therefore, lanthanum phosphate is recommended as a
prospective barrier coating on crucibles and substrates used for high temperature processing of uranium and its alloys.

Stainless steel coupons and samples covered with plasma spray-coated LaPO$_4$ were used as test specimens to evaluate the efficacy of the coating to prevent corrosion of the substrate by uranium using differential thermal analysis. Details of the corrosion test and results of the test are presented in this chapter.

5.2 Experimental method

Chemical reaction of LaPO$_4$ with uranium was evaluated by DTA using stainless steel specimens coated on all sides with LaPO$_4$. Atmospheric plasma spray technique was used to apply the coatings as detailed in chapter 4. LaPO$_4$ powder (38-75 µm) was used as the starting material. Samples (4 x 4 x 4 mm) of SS coated with LaPO$_4$ on all sides were used as the test specimens. Plasma spraying was carried out at 20 kW using a mixture of argon and nitrogen. For corrosion experiment, the coated specimen was sandwiched between two uranium discs of about 3 mm diameter and about 2 mm thick (weight of each U disc was about 0.27g) and placed in a cylindrical sintered alumina crucible (6 mm internal diameter and 12 mm height) of the DTA equipment. The sample was heated in helium gas at a heating rate of 10 °C min$^{-1}$ and the thermal energy change was continuously recorded with time. The sample was heated to 1200 °C so as to ensure that uranium was in the molten state and was held isothermally at that temperature for 2 hours. It was then cooled to room temperature.

5.2.1 Compatibility evaluation of LaPO$_4$ with molten uranium

Result of a typical DTA experiment is summarized in figure 5.1. It is evident that LaPO$_4$ does not react with uranium. The DTA peaks observed are characteristic of the phase transition of different phases of uranium metal and melting of uranium. The endothermic peaks seen during heating cycle correspond
to the transition of phase transition and melting of uranium. The endothermic peak observed at about 680 °C corresponds to the transition of the orthorhombic phase of uranium (alpha uranium) to the beta-phase of uranium. The beta phase transforms to the body centered cubic phase (gamma) at about 799 °C. The endothermic peak occurring at about 1137 °C corresponds to the melting of uranium. During the cooling cycle, all these peaks appear as exothermic peaks. No other peak corresponding to any reaction between LaPO$_4$ and U is observed.

The sample, after DTA experiment, was carefully cross sectioned using precision diamond wheel cutting machine. Cross-sectioned sample was mounted by cold setting epoxy resin and allowed to cure at room temperature for 24 hours. The mounted samples were polished using emery papers with various grit sizes and final polishing was done with diamond paste of grade 3–0.25 µm size. DTA experiment and metallographic sample preparation including cutting, mounting and polishing were carried out in the metallurgical laboratory of the Radiometallurgy Division of BARC exclusively meant for handling radio-active samples.

The coating-substrate interface was analyzed using SEM and it is found to be intact. In case of any chemical reaction between molten uranium and lanthanum phosphate, the reaction should have been spread over the entire surface of the coatings. Therefore, EDX area scan of elements over the total surface of the coating was carried out. Figure 5.2 shows EDX spectrum of the entire area of the coating-substrate interface after DTA experiment. The area scan shows characteristic spectral lines of La, P, O and Fe (from substrate) as the constituents. Uranium peaks are observed to be below the detectable limit of the instrument. Figure 5.3 shows SEM-EDX line spectrum of the coating-substrate interface after DTA experiment. The EDX spectrum shows characteristic lines of La, P, O and iron (from the substrate) and uranium is found to be below the detectable limit as evident from the line spectrum.
Figure 5.1 DTA experiment of interaction between LaPO$_4$ and uranium

Although the concentration of lanthanum near the coating-substrate interface is seen to be very low (Fig. 5.3), this cannot be attributed to the depletion of lanthanum by reaction with molten uranium. Depletion of lanthanum
due to corrosion by uranium should have led to coating failure. However, the coating integrity is seen to be intact after the DTA experiment. Further, any reaction between lanthanum and uranium should be reflected in the EDX spectrum, which shows uranium below detectable limit. In this context, it is very pertinent to note that EDX analysis does not give quantitative idea of the elements present in the sample, although it gives a fairly semi-quantitative estimate of the composition. This is particularly applicable when analyzing samples containing rough particles, uneven surfaces, porosity, etc as in the case of plasma sprayed coatings. In such cases, intensities of characteristic x-rays emitted from different elements may not be commensurate with their respective concentrations.

Figure 5.3 The SEM-EDX line spectrum of coating-substrate interface after DTA experiment

Milos Miler and Breda Mirtic (2013) have carried out detailed study to estimate the reliability of EDX analysis for identification of various natural and anthropogenic metal-bearing phases in polished and rough particle samples of stream sediments. According to these authors, composition could not be reliably
determined for 62% of mineral phases by EDX. It is therefore concluded that the low concentration of lanthanum near the substrate coating interface is not due to any reaction with uranium, but is due to sample features and instrumental limitation as explained above. Hence, lanthanum phosphate coatings can be used effectively to protect the underlying substrate against corrosion of uranium. The specimen surface after the DTA experiment did not show any uranium particle sticking on the surface. This is due to the low wettability of LaPO$_4$ towards molten uranium.

5.3 Phase instability in the corrosion resistance coating

Although LaPO$_4$ melts congruently at about 2040 °C, phase instability in plasma spray deposited LaPO$_4$ is expected because LaPO$_4$ is a line compound (Park et al. 1983) and even small deviations in stoichiometry can lead to formation of La$_3$PO$_7$ and La$_2$P$_4$O$_{13}$. This has been confirmed by thermal stability studies on plasma sprayed LaPO$_4$ coatings and melt-quenched spheroids presented in chapter 3 and 4. It was observed that the coatings and spheroidized samples contained secondary phases such as La$_3$PO$_7$ and La$_2$P$_4$O$_{13}$. However, subsequent thermal treatment of the coating and plasma spheroidized particles resulted in the recombination of the secondary phases to give monazite phase of LaPO$_4$.

It is interesting to note that presence of secondary phases did not affect the efficacy of plasma deposited LaPO$_4$ coatings in protecting the substrate against corrosion by uranium metal. However, as discussed earlier, these secondary phosphates recombine after annealing at 1100 °C for two hours. The DTA was carried out from room temperature to 1200 °C with a 2 hour isothermal hold at 1200 °C. At this stage, La-poly and La-oxy phosphates would have recombined to form monazite as confirmed by experimental results reported in chapter 3. Hence, it may be concluded that monazite phase is formed before melting of
U-disc and monazite surface of the coating resists the molten metal corrosion. Another interesting aspect that needs to be noted is that recombination of these secondary phases during thermal treatment does not lead to any crack formation or disrupts the coating integrity. The coating-substrate interface is found to be intact after the DTA experiment, showing that the coating offered sufficient protection to the underlying substrate against corrosion of uranium.

In summary, it may be concluded that plasma sprayed LaPO$_4$ coatings offered sufficient protection to the underlying substrates against corrosion by molten uranium. Since LaPO$_4$ has a definite melting point and melts congruently, it can be deposited by plasma spray technique. However, LaPO$_4$ phase has only a narrow temperature range of stability above its melting point. Control of particle temperature during plasma spraying is, therefore, important to control the formation of secondary phases. In plasma spraying, it is very difficult to control the particle temperature in a narrow range, especially while depositing ceramic materials. Formation of secondary phases like La$_3$PO$_7$ and La$_2$P$_4$O$_{13}$ is unavoidable; however, these secondary phases recombine to form LaPO$_4$ during in-service thermal treatment without crack formation and disrupting the coating integrity. Therefore, plasma sprayed LaPO$_4$ coatings can be recommended for barrier applications to protect the underlying substrate against corrosion by molten uranium and its alloys.

**5.4 Summary**

Chemical reaction of LaPO$_4$ with uranium was evaluated by differential thermal analysis (DTA) using a stainless steel specimen coated on all sides with LaPO$_4$ using atmospheric plasma spraying. The coating-substrate interface was found to be intact after the DTA experiment. Post analysis of the coating by SEM and EDX showed that there was no reaction between uranium and lanthanum phosphate and the coating integrity was found to be intact. Hence, it can be
concluded that the coating offered sufficient protection to the underlying substrate against corrosion by uranium.