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Preparation and characterisation of platinum and platinum–iridium coated titanium electrodes

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Abstract

Metallic coatings of Pt and Pt–Ir were prepared by the thermochemical glazing process on titanium substrates for application as electrodes in the electrolytic dissolution of nuclear fuels. Titanium substrates with a RuO_2–TiO_2 single layer were applied with Pt and Pt–Ir chemical solutions and heat treated in vacuum at different temperatures between 973 and 1473 K for 1 h. The physical characterisation by SEM/EDX, XRD and SIMS indicated the presence of adherent and smooth metallic coatings of Pt–Ti and Pt–Ir containing intermetallic compounds of Ti, Pt and Ir. Electrochemical polarisation studies carried out in 1 M HNO_3 at room temperature showed that the specimen prepared at 1373 K had a better electrochemical performance in comparison with Pt sheet electrodes. Significant changes in the open circuit potential (OCP) and the polarisation behaviour of the electrodes were noticed. The life assessment in a simulated reprocessing test solution of boiling 10 M HNO_3 showed excellent performance of the Pt–Ir layered electrode in comparison with conventional mixed oxide coated titanium (MOCTA) electrodes. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Electrochemical methods are one of the promising ways of dissolving and purifying the spent nuclear fuel from nuclear reactors compared to the conventional chemical methods. A number of electrochemical processes [1–5] are currently employed world wide due to their simplicity, high efficiency and easy control over the process including remote operation. They are electrolytic dissolution and conditioning, electrolytic partitioning and purification, electrolytic production of uranous (U^{4+}) ions, electrolytic destruction of organics, nitric acid and radioactive wastes etc. All the above processes use nitric acid from dilute to concentrated, from room temperature to boiling condition, and with the addition of redox systems for improving the current efficiency. The success and current efficiency of the electrochemical processes mainly depend on the durability or the corrosion resistance of the electrodes, electrocatalytic activity or the low over-voltage of the coatings for the desired rate determining electrochemical reaction, and high conductivity facilitating operation of the electrolytic cells at high current densities. In addition, (i) to avoid minimum interruption to the operation, (ii) to avoid frequent replacement or addition of new electrodes in a radioactive environment, and (iii) to have improved current efficiency, longer life of the electrodes used is of paramount importance. Currently, platinum electrodes are being used in the above applications. However, it has been reported [1] that platinum undergoes corrosion at high current densities of operation in nitric acid medium at high temperatures. Moreover, platinum is expensive considering the cost involved in operating the plant with many unit operations. The failed platinum electrodes in a highly contaminated state cannot be refabricated for further use and also increased the solid waste volume. All this necessitated the development of economical platinised electrodes with corrosion resistant substrates providing high efficiency on par with platinum electrodes for effective use in the plant.

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Platinised tantalum and titanium electrodes were used in many electrochemical applications in the reprocessing plants [6–8]. The details of preparation and performance evaluation of such electrodes are scarce in the literature and in most cases they are available as patents. Hence, there was a need to take up detailed investigations for developing new electrodes and electrode coatings which can show improved performance in the severe conditions encountered in reprocessing plants. Mixed oxide coated titanium anodes (MOCTA) were developed [9,10] for application as electrodes in the electrochemical processes employed for the dissolution and the purification of the (U,Pu)C fuel of the fast breeder test reactor (FBTR) at Kalpakkam, India. MOCTA belongs to the category of dimensionally stable anodes (DSA) which are basically a mixture of oxides of Ru, Ti, Pt, Rh, Ir, Sn and Pd coated over the surface of Ti, Ta, W, Cr, or Zr [11–14]. The MOCTA electrodes are titanium substrates coated with RuO_2 and TiO_2, with or without an overlay of PtO_2. For the electrolytic dissolution of the ceramic (U,Pu)C fuels, severe corrosive conditions are encountered with boiling nitric acid containing redox ions [5]. The presently used composition of the MOCTA coating of RuO_2/TiO_2 with an overlay of PtO_2 are found to operate only for durations up to 230 h [9] while electrolytic tests were carried out in a simulated reprocessing solution. To increase the life of the electrode coatings, a new approach was made in the present work to develop metallic coatings containing Pt and Ir with an intermittent MOCTA layer on a titanium substrate. The electrodes prepared were characterised by scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), and secondary ion mass spectrometry (SIMS). The electrochemical polarisation behaviour of the electrodes was studied in a nitric acid medium under anodic and cathodic conditions, and the life assessment of the electrode was carried out in a simulated reprocessing solution containing uranium and other redox ions. This paper describes the results of the present investigation.

2. Experimental work

Commercially pure (CP) titanium was used in the present investigation. Analytical grade chemicals were employed for all purposes.

2.1. Preparation of titanium surfaces

The main problem faced in obtaining good adhesion of the coating on titanium was the presence of the tough natural titanium oxide film formed on the surface, and its chemical composition which depends on the conditions of formation. An adherent electrode coating over titanium can be obtained only if this natural titanium oxide film is removed or is replaced by another film that does not interfere with adhesion. Several procedures such as chemical etching in acid solutions and electrolytic etching in different baths are usually followed for the preparation of titanium for adherent deposition of metals.

For the present work, commercially pure titanium in mesh form was cut into 50 mm × 50 mm, and cylindrical electrodes of 45 mm diameter and 50 mm length, both with a lead of titanium for electrical connection. Specimens of 10 mm × 10 mm × 2 mm were also prepared from a titanium sheet. These specimens were sand blasted for mechanical roughening of the surface to improve the adherence of the coating. Degreasing of titanium was carried out to remove oil, grease and other foreign materials using organic solvents like acetone or trichloroethylene under boiling conditions for 10 min which was then air dried. The degreased surface was etched with a 10% sodium hydroxide solution, and thoroughly washed with distilled water. The final surface preparation of titanium mesh was done in a mixture of HF and HNO_3 solutions, and then washed with distilled water and air dried. The surface thus prepared has been reported to provide an excellent configuration for the development of coatings with good adherence [14].

2.2. Coating solution preparation

The homogeneity and the adherence of the coating also depend on the concentration and viscosity of the coating solution. The solvents generally preferred for mixing the chloride salts of ruthenium or titanium are hydrochloric acid and *n*-butyl alcohol. It was found that coating with *n*-butanol gives better adherence than hydrochloric acid [14]. Hence, an appropriate amount of $RuCl_3$ was dissolved in *n*-butanol to prepare a 0.1 M solution. This standard solution was mixed with an appropriate mole percentage of tetrabutyl titanate to give a mole ratio of 40:60 of $RuO_2:TiO_2$, as this ratio is found to exhibit better dimensional stability over others for electrochemical reactions occurring at potentials higher than an oxygen evolution [14]. Similarly, solutions of chloroplatinic acid mixed with iridium chloride and *n*-butanol were prepared.

2.3. Coating solution application and thermochemical treatment

The solution thus prepared was applied on the pretreated titanium substrate using a soft painting brush in such a way that no cloud formation or discontinuous layers are present due to the excess solution applied over the surface. Then, the sample was allowed to dry at ambient temperature for about 10 min. Thereafter it was heated at 623 K for 15 min in a muffle furnace in order to dry the coating solution applied over the surface. After the application of a single layer of RuO_2/TiO_2 coating, solutions of chloroplatinic acid mixed with *n*-butanol was applied over the dried surface with repetitive drying at 623 K for 15 min in order to produce the required thickness of Pt coating. Following this, solutions of chloroplatinic acid mixed with iridium chloride and *n*-butanol were applied over the dried surface with repetitive drying at 623 K for 15 min in order to produce the required thickness of Pt–Ir coating. Thermochemical treatment of these coated Ti substrates was carried out in a high-temperature high-vacuum furnace, GCA made, USA, at 10^{-6} bar, at different temperatures viz. 973, 1173, 1273, 1373 and 1473 K in order to produce bright, glazed surfaces containing Pt and Pt–Ir alloy. These 'thermochemically glazed (MOCTAG)' electrodes would possess higher electrocatalytic activity and better adherence of the coating in comparison with conventional MOCTA electrodes prepared at low temperatures (773 K) in an open furnace.

2.4. Physical characterisation of MOCTAG coatings

Specimens of 10 mm × 10 mm × 2 mm sizes with MOCTAG coatings were examined for the surface morphology in a Philips made SEM coupled with EDX. The examination of the cross-section of the electrodes was carried out after electroplating the surface with nickel. Ti-Kα, Ru-Lα and -Lβ, Pt-Lα and -Mα, and Ir-Lα and -Mα lines were analysed for the intensity of the above alloying elements present in the coating. X-ray diffraction was performed on the specimens, using Cu-Kα radiation in a Philips made diffractometer, for the phases present. SIMS analyses of the specimens were carried out using a CAMECA IMS-4F system using a Cs^+ primary ion beam at 10 kV. The intensity profile of Ti, O, Pt, Ru and Ir was obtained with respect to the time of sputtering.

2.5. Electrochemical polarisation studies

Anodic and cathodic polarisation studies were carried out to understand the polarisation behaviour of the MOCTAG electrodes prepared at different temperatures. The experiments were conducted by the potentiodynamic method in 1 M HNO_3 medium at room temperature (298 K) and 323 K. Pure titanium was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode to measure the electrode potential. A sweep rate of 0.167 mV/s was used for applying the potential from the open circuit potential (OCP) in anodic and cathodic directions. Prior to the potential sweep, the electrodes were immersed in the electrolyte for an hour in order to establish a steady-state condition between the electrodes and the electrolyte. The open circuit potential (OCP) was measured after this period. From OCP an external potential was applied using a Germany made, Wenking Potentiostat POS 72, and the corresponding current values were measured. For comparison purpose, electrodes of platinum sheet and Pt electroplated on Ti were also tested under similar conditions.

2.6. Life assessment of MOCTAG coatings

Cylindrical electrodes of 45 mm diameter and 50 mm length were prepared for life assessment experiments. Titanium was used as cathode, and both titanium and MOCTAG were separated using a polytetrafluoroethylene disc. A simulated reprocessing solution of nitric acid containing uranium and other redox ions was prepared as per the composition shown in Table 1. A dc voltage regulator was used to apply the cell potential to the electrodes immersed in the simulated boiling reprocessing test solution. The cell potential and current were monitored periodically while the electrolysis was continued. The cell voltage was maintained at 2 V at a current density of 128 A/m^2 for the MOCTAG electrodes. The corresponding initial current for this potential was 1.4 A. Similar test conditions were applied for the life assessment of MOCTA (at a current density of 65 A/m^2) and modified MOCTA with PtO_2 coating (at a current density of 90 A/m^2).

3. Results and discussion

3.1. Analysis of the MOCTAG surface

Fig. 1(a) shows the typical cracked-mud morphology of the conventional MOCTA electrodes. The presence of cracks, and the anchor-shaped sharp edges of the oxide slabs facilitate efficient gas evolution in the electrochemical processes. In comparison with this, Fig. 1(b) shows the smooth and compact PtO_2 overlayer present in platinised MOCTA coatings. The details of the MOCTA electrode preparation, characterisation and application have been already published by the authors [9]. Figs. 1(c) and (d) show the general appearance of the MOCTAG layer developed on the surface for both Pt

Table 1
Composition of the simulated reprocessing solution

Uranium as uranyl nitrate	70 g/l
Cerium as cerium nitrate	0.978 g/l
Iodine as KI	0.0219 g/l
Palladium[a]	0.389 g/l
Ruthenium as RuO_2[a]	0.837 g/l
Silver as silver nitrate[b]	0.05 M
Nitric acid	10 M

[a] Possible fission products.

[b] Possible catalytic redox ions.

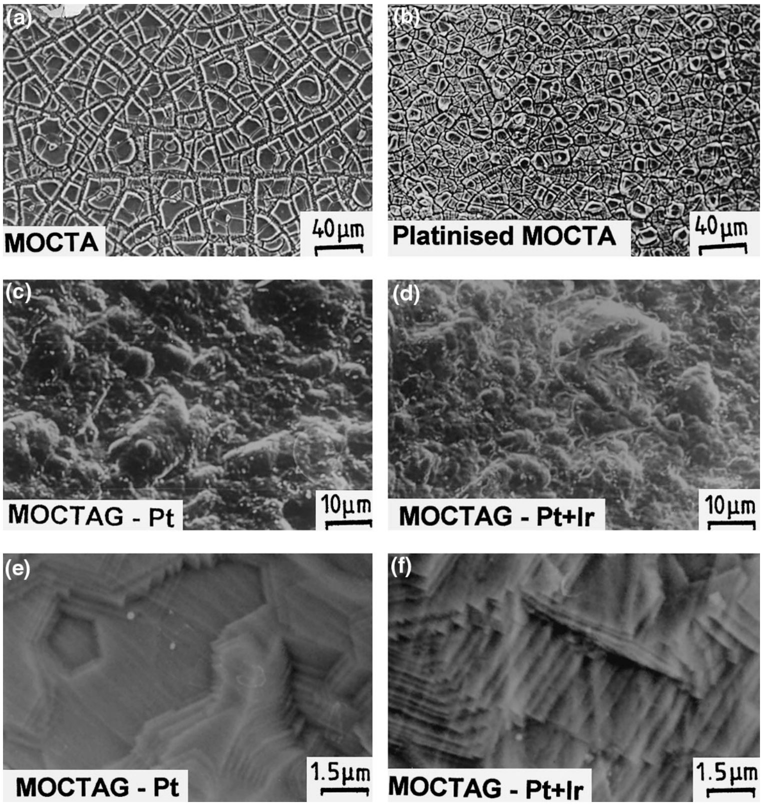

Fig. 1. (a) Cracked-mud morphology of MOCTA, (b) fine-grained smooth platinised MOCTA, (c) appearance of MOCTAG with Pt, and (d) appearance of MOCTAG with Pt–Ir, (e) and (f) ordered smooth metallic layers of Pt and Pt–Ir.

and Pt–Ir compositions. In addition to the general appearance seen in Figs. 1(c) and (d), significant changes in the morphology were noticed at the surface in various locations. A well-developed and ordered structure was noticed for both Pt and Pt–Ir layered coatings (Figs. 1(e) and (f)). Such a structure formation could be attributed to the smooth transformation of the coating solution into an ordered metallic layer consisting of intermetallic Pt–Ti and Pt–Ir phases like $TiPt_8$, $TiPt_3$, Ti_3Pt_5, TiPt, IrPt, TiIr etc. [15,16]. The EDX analysis of the specimens confirmed the significant presence of Pt and Pt-Ir on the surface in comparison with the conventional MOCTA electrode specimens. XRD analysis confirmed the presence of intermetallic phases in the metallic layer developed. Table 2 gives the details of the phase analysis carried out with the specimens and the various phases present in the coatings. SIMS analysis indicated the presence of Pt, Ru and Pt, and Ru and Ir on the surface for both types of electrodes. Fig. 2(a)–(c) shows the plots of intensity against the sputtering time for the Pt, Pt–Ir

Table 2
XRD analysis of coated electrodes[a]

Electrode	Temperature of preparation (K)	Phases present
MOCTA	773	TiO_2 (rutile), RuO_2, Ti, Ru
Platinum coated titanium	973	Ti, TiO_2 (rutile), TiPt (S), Ti_3Pt_5 (S), RuO_2 (W)
	1173	Ti, TiO_2 (rutile), TiPt (S), Ti_3Pt_5 (S), Ru (W)
	1373	Ti, TiO_2 (rutile), TiPt (S), Ti_3Pt_5 (S), Ru (W), Pt (S)
	1473	Ti, TiO_2 (rutile), TiPt (S), Ti_3Pt_5 (S), Pt (W)
Pt–Ir coated titanium	973	Ti, TiO_2 (rutile), TiPt (S), Ti_3Pt_5 (S), RuO_2 (W)
	1173	Ti, IrO_2 (rutile), TiPt (W), RuO_2, IrTi
	1373	Ti, TiO_2 (rutile), Ti_3Pt_5, Ir (W), TiPt (S), TiIr (S), $TiIr_3$ (W)
	1473	Ti, TiO_2 (rutile), Ti_3Pt5, Ir (W), TiPt (S), TiIr (S),$TiIr_3$ (W)

[a] S – strong peak; W – weak peak.

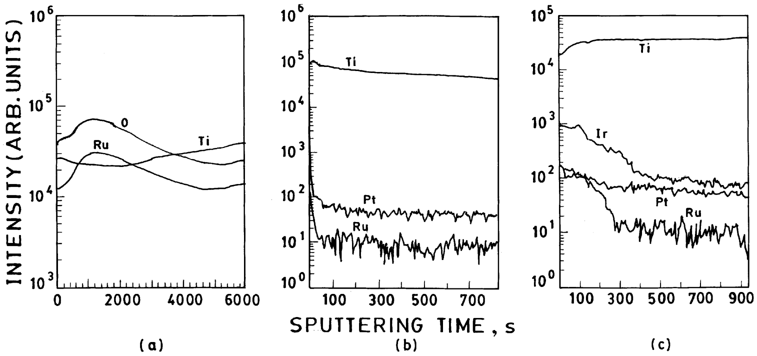

Fig. 2. SIMS analysis of (a) MOCTA, (b) Pt and (c) Pt–Ir coated Ti substrate.

and MOCTA coated Ti substrates. The uniform distribution of Pt- and Ir-rich alloy phases was also noticed during the analysis.

3.2. Polarisation behaviour of MOCTAG electrodes

Fig. 3 shows the variation of OCP with the type of coating present on the titanium surface, in comparison with a Pt sheet. It can be noticed that the OCP values of the Pt and Pt–Ir layered Ti electrodes were much active compared to those of a Pt sheet and Pt electroplated on Ti electrodes. Figs. 4(a) and (b) show the anodic polarisation curves for conventional MOCTA, MOCTAG and Pt sheet electrodes. Significant changes in the polarisation behaviour of the MOCTAG electrodes, depending on the heat treatment, can be noticed. It was observed that the MOCTAG electrodes prepared at 1273, 1373 and 1473 K showed better polarisation behaviour which was superior for the MOCTA electrode, and tending towards the polarisation behaviour of the Pt sheet electrode. Fig. 5 shows the anodic polarisation curves of MOCTA, in comparison with MOCTAG electrodes prepared at 973, 1173 and 1373 K, and tested at 323 K in 1 M HNO_3. In comparison with MOCTA, the MOCTAG electrodes showed better polarisation behaviour even at a lower current density (MOCTA – 1 A/m^2, MOCTAG (Pt) – 0.2 A/m^2, MOCTAG(Pt/Ir) – 0.1 A/m^2, whereas for Pt sheet it was 0.02 A/m^2, the current density at which stable polarisation was

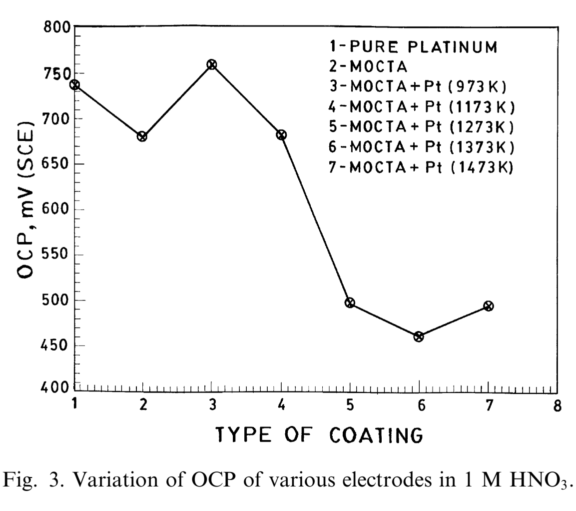

Fig. 3. Variation of OCP of various electrodes in 1 M HNO_3.

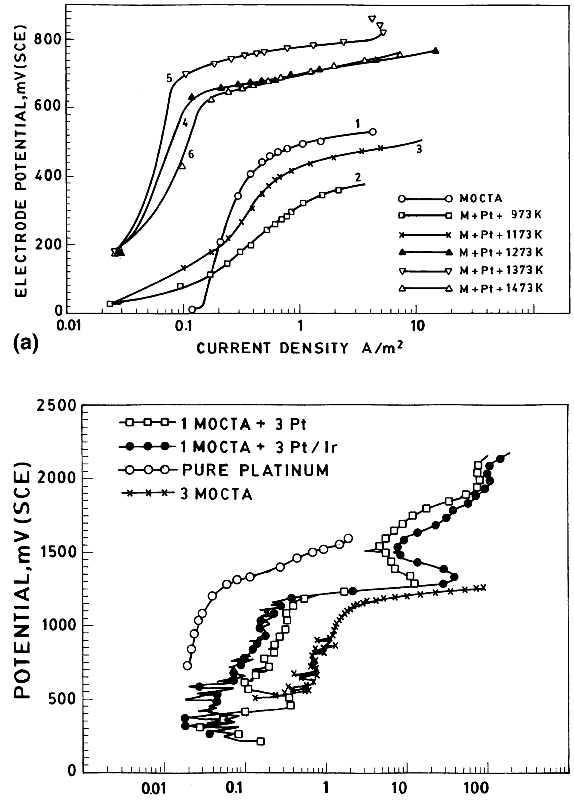

Fig. 4. (a) and (b) Anodic polarisation curves of electrodes at 298 K in 1 M HNO_3.

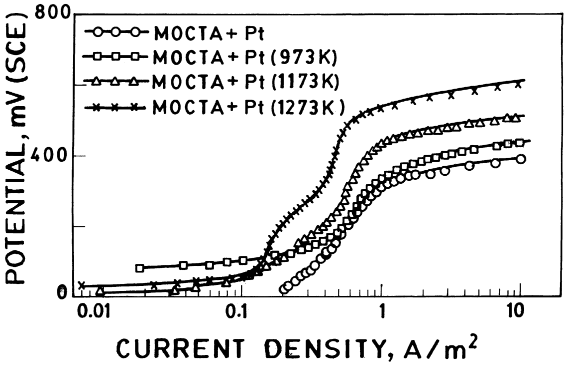

Fig. 5. Anodic polarisation curves of electrodes at 323 K in 1 M HNO_3.

noticed). The degradation of the MOCTAG surface was insignificant after anodic polarisation studies in 1 M HNO_3, as shown in Figs. 6(a) and (b). From the above results the performance of the MOCTAG, particularly the one prepared at 1373 K, was found to exhibit better performance than the conventional MOCTA electrodes.

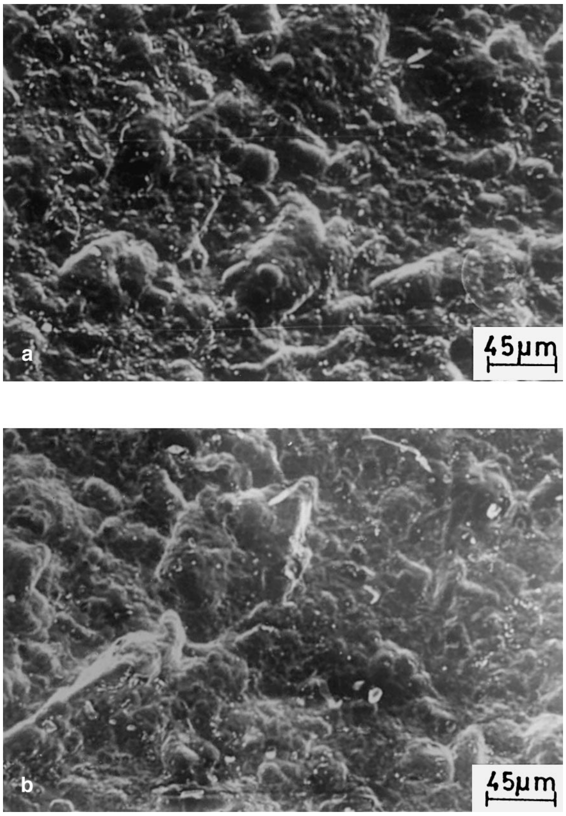

Fig. 6. Insignificant degradation at surface for (a) MOCTAG with Pt, and (b) MOCTAG with Pt–Ir, after anodic polarisation in 1 M HNO_3.

3.3. Life assessment of MOCTAG electrodes

The results of the life assessment test showed that the MOCTA electrode worked satisfactorily up to 215 h at an operating current density of 60 A/m^2. Beyond this, the cell current decreased to negligible values indicating that the electrode failed. The platinised MOCTA worked satisfactorily up to 230 h at an operating current density of 80 A/m^2. This could be due to the high catalytic activity of Pt, and the fine grained oxide structure present at the surface compared to cracked-mud morphology of MOCTA as shown in Fig. 1(a). In the case of MOCTAG, the electrode continued to work up to 1540 h at an operating current density of 128 A/m^2 without any failure (Fig. 7). This indicated the superiority of the Pt–Ir metallic coating developed by the thermochemical-glazing process in comparison with MOCTA and platinised MOCTA electrodes. The high current density of MOCTAG could be attributed to the better conductivity and high electrocatalytic activity of Pt, and the presence of intermetallic Pt, Ti and Ir alloy phases. In the case of MOCTA electrodes the oxide coatings produce lesser conductivity. The long life of this electrode is due to the strong adhesion of the metallic coatings prepared at high temperature in comparison with the oxide coated electrodes developed at temperatures $\leqslant 773$ K. For MOCTA electrodes it was found that the oxide slabs got detached from the surface and selective dissolution occurred at the surface due to poor adhesion of the coating, and thus the useful life of these electrodes was only about 215 h in a simulated reprocessing solution [9].

3.4. The role of MOCTAG in electrolytic dissolution of nuclear fuels

In the electrolytic dissolution of refractory nuclear fuels containing uranium and plutonium the dissolution takes place as per the following reactions [3]:

$$PuO_2 \Longleftrightarrow PuO_2^+ + e, \quad E^0 = 1.58 \text{ V (SHE)}, \qquad (1)$$

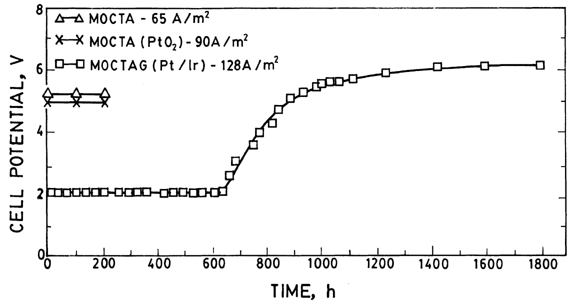

Fig. 7. Performance of electrodes during electrolysis of simulated reprocessing test solution.

$$\mathrm{PuO_2^+} \Longleftrightarrow \mathrm{PuO_2^{2+}} + \mathrm{e}, \quad E^0 = 0.92\ \mathrm{V\ (SHE)}, \qquad (2)$$

$$\mathrm{PuO_2} \Longleftrightarrow \mathrm{PuO_2^{2+}} + 2\mathrm{e}, \quad E^0 = 1.24\ \mathrm{V\ (SHE)}. \qquad (3)$$

The dissolution proceeds according to

$$\mathrm{PuO_2(IV)} \Longleftrightarrow \mathrm{PuO_2^+(V)} \Longleftrightarrow \mathrm{PuO_2^{2+}(VI)}.$$

Considering less probability for reaction (3) involving greater than one electron transfer, the dissolution is always considered to proceed through reaction (1). According to Horner [17] fast dissolution can occur at a solution potential of 1.38 V in nitric acid medium containing cerium ions. The following eletrocatalytic reagents [18,19] can be chosen for an effective dissolution kinetics of the above reactions:

$$\mathrm{Ce^{3+}} \Longleftrightarrow \mathrm{Ce^{4+}} + \mathrm{e}, \quad E^0 = 1.61\ \mathrm{V\ (SHE)}, \qquad (4)$$

$$\mathrm{Ag+} \Longleftrightarrow \mathrm{Ag^{2+}} + \mathrm{e}, \quad E^0 = 1.92\ \mathrm{V\ (SHE)}. \qquad (5)$$

The net anodic reactions occurring at MOCTAG surface in the cell are

$$\mathrm{Ag^+}\text{(in solution)} \Longleftrightarrow \mathrm{Ag^{2+}}\text{ (turns solution into darkish brown colour)} + \mathrm{e}\text{ (to MOCTAG)},$$

$$\mathrm{PuO_2}\text{ (IV) (solid)} + \mathrm{Ag^{2+}}\text{ (in solution)} \Longleftrightarrow \mathrm{PuO_2^+}\text{(V) (in solution)} + \mathrm{Ag^+}\text{(to solution)},$$

$$\mathrm{PuO_2^+}\text{(V) (in solution)} + \mathrm{Ag^{2+}} \Longleftrightarrow \mathrm{PuO_2^{2+}}\text{(VI) (in solution)} + \mathrm{Ag^+}\text{+e(to MOCTAG)}.$$

The rate determining step in enhancing the dissolution reaction is therefore the rate of electron transfer between $\mathrm{PuO_2}$ (IV) and $\mathrm{Ag^{2+}}$ to produce $\mathrm{PuO_2^+}$(V) and $\mathrm{Ag^+}$ ions. It has been reported [3] that the electron exchange rate of the $\mathrm{Ag^+/Ag^{2+}}$ redox system is very high compared to all other redox systems including that of cerium. MOCTAG acts as an indefinite source for the regeneration of $\mathrm{Ag^{2+}}$ ions required for the oxidation of $\mathrm{PuO_2}$ (IV) to $\mathrm{PuO_2}$ (V) and then to $\mathrm{PuO_2}$ (VI). In the case of carbide fuels the additional advantage of using MOCTAG electrodes could be the oxidation of organics such as oxalic acid, mellitic acid etc. generated during the dissolution into gaseous species like CO, $\mathrm{CO_2}$ etc. In this case, the $\mathrm{Ag^{2+}}$ ions regenerated at the MOCTAG reacts with the water to form oxidising and reactive species like OH: radicals represented as [O]:

$$2\mathrm{Ag^{2+}} + \mathrm{H_2O} \Rightarrow 2\mathrm{Ag^+} + 2\mathrm{H^+} + [\mathrm{O}].$$

The reactive species react with the organics to oxidise them into gaseous species like CO, $\mathrm{CO_2}$ etc.

$$\text{Organics} + [\mathrm{O}] \Rightarrow \mathrm{CO_2} + \mathrm{CO} + \mathrm{H_2O}.$$

This helps in avoiding emulsification and flooding problems during the subsequent solvent extraction process. Thus, for the complete dissolution of U and Pu-based nuclear fuels, the presence of kinetically active redox systems and a non-corroding catalytic electrode providing an indefinite source of electrons for activating the dissolution process are necessary. In this case, both MOCTA and MOCTAG electrodes proved to be candidate materials for application in the electrolytic dissolution of nuclear fuels. However, considering the life of the electrodes for such severe corrosive environment, MOCTAG is recommended as it possesses longer service life.

4. Conclusions

The results of the present investigation suggested the following conclusions.

(i) Pt and Pt–Ir layered titanium electrodes prepared by the thermochemical glazing process showed better electrochemical properties compared to conventional MOCTA electrodes during OCP measurements and anodic polarisation studies; the electrode prepared at 1373 K showed superior properties.

(ii) SEM/EDX examinations indicated better adhesion of the layer with Pt and Pt–Ir, and the XRD analysis confirmed the presence of intermetallic Pt–Ti and Pt–Ir alloy phases at the surface. SIMS analysis indicated the distribution of Pt- and Ir-enriched phases on the surface.

(iii) Life assessment of the electrodes during electrolysis in a severe corrosive environment showed that these electrodes possessed a longer life compared to conventionally platinised electrodes.

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References

[1] F. Baumgärtner, H. Schmieder, Radiochim. Acta 25 (1978) 191.
[2] H. Matzke, Science of Advanced LMFBR Fuels, North-Holland Physics Publishing Company, Amsterdam, 1986, p. 623.

[3] L.A. Bray, J.L. Ryan, in: Actinide Recovery from Waste and Low Grade Sources, J.D. Navrutil, W.W. Schulz (Eds.), Harwood, New York, 1982, p. 129.
[4] A. Palamalai, S.K. Rajan, A. Chinnusamy, M. Sampath, P.K. Verghese, T.N. Ravi, V.R. Raman, G.R. Balasubramanian, Radiochim. Acta 55 (1991) 29.
[5] A. Palamalai, PhD thesis, Madras University, 1988.
[6] L.A. Bray, J.L. Ryan, E.J. Wheelwright, Development of the CEPOD Process for Dissolving Plutonium Oxide and Leaching Plutonium from Scrap or Wastes, Report No. PNL-5657 UC-70, Pacific Northwest Laboratory, Washington, 1985.
[7] He Jianyu, Zhang Qingxuan, Luo Longjun, Tian Baosheng, in : Proceedings of the 3rd International Conference on Nuclear Fuel Reprocessing and Waste Management RECOD-91, Sendai, Japan, 1991.
[8] H. Schmieder, H. Goldacker, U. Galla, M. Heilgeist, M. Kluth, G. Petrich, in: Proc. of the Conf. on Fuel Reprocessing and Waste Management, American Nuclear Society Topical Meeting, Jackson, Wyoning, 1984.
[9] U. Kamachi Mudali, R.K. Dayal, J.B. Gnanamoorthy, Nucl. Technol. 100 (1992) 395.
[10] U. Kamachi Mudali, R.K. Dayal, J.B. Gnanamoorthy, S.K. Rajan, A. Palamalai, in: Proc. of the Int. Symposium on Thermochemistry and Chemical Processing, Kalpakkam, 1991, p. 293.
[11] H.B. Beer, British patent, 964, 913.
[12] H.B. Beer, in: U. Landu, E.Yeager, D.Kortan (Eds.), Electrochemistry in Industry, Plenum, New York, 1982, p. 19.
[13] S. Trasatti, Electrodes of Conductive Metallic Oxides – Parts A & B, Amsterdam, 1980.
[14] U. Kamachi Mudali, M. Tech. thesis, IIT Bombay, 1984.
[15] B.C. Beard, P. Ross Jr., J. Electrochem. Soc. 133 (1986) 1839.
[16] T. Massalski, Binary Alloy Phase Diagrams, 2nd ed., American Society for Metals, ASM, Philadelphia, PA, 1990.
[17] D.E. Horner et al., USERDA Report ORNL/TM-4716, 1977.
[18] A. Palamalai, S.K. Rajan, G.R. Balasubramanian, Trans. SAEST 22 (1987) 203.
[19] F.J. Poncelet, M.H. Mouliney, V. Decobert, M. Lecomte, in: Proc. of the 4th Int. Conf. on Nuclear Fuel Reprocessing and Waste Management RECOD-94, vol. II, British Nuclear Industry Forum, London, UK, 1994.