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Electrochemical studies of Ir coating deposition from NaCl-KCl-CsCl molten salts

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ABSTRACT

In this paper, the electrochemical behavior of Ir^{3+} ions in melting NaCl-KCl-CsCl-$IrCl_3$ and the major kinetic parameters were investigated by transient and steady electrochemical techniques from 823 K to 913 K. Effects of the electrochemistry of Ir^{3+} ions on the microstructure of Ir coatings were also discussed. The electrochemical reduction of Ir^{3+} ions from the melts was the diffusion-controlled and irreversible reaction with exchange of three electrons at 823–883 K and converted to be a quasi-reversible one with the temperature increasing to 913 K. The major kinetic parameters of Ir^{3+}/Ir couples, the diffusion coefficient D_0 and exchange current density j_0, respectively increased from 2.4×10^{-6} cm^2/s to 9.2×10^{-6} cm^2/s and from 5 mA/cm^2 to 16 mA/cm^2 with the temperature. With the temperature and applied cathodic potential decreasing, the microstructure of Ir coatings converted from the coarse and preferential oriented columnar grain structure to the fine and unoriented dispersive grain structure.

1. Introduction

Metal iridium (Ir) is considered as one of the most promising oxidation resistance materials at elevated temperatures due to its high melting point and low oxygen permeability and good mechanical properties [1–4]. Ir and its alloys thus have been widely used as the oxidation resistance coatings for high temperature structural applications, such as satellites liquid rocket engines and leading edges of hypersonic aircraft [5–7].

Ir coatings have been prepared by versatile approaches [8–12], among which electrodeposition was the most efficient and high-quality one for fabricating Ir coatings on complex-shaped components [13–18]. And nontoxic ternary NaCl-KCl-CsCl melts were widely used as electrolytes in the Ir electrodeposition [19]. Dense and continuous Ir coatings on various substrates have been prepared successfully from the NaCl-KCl-CsCl melts by Zhu and Huang [20–30]. According to them, the morphology of Ir coatings is decided by the deposition conditions, including temperature, current density and concentration of Ir^{3+} ions. Moreover, according to Saltykova N. A. [31,32], while the electrochemical reduction of Ir^{3+} ions in ternary melts is totally irreversible at 773–873 K, it will be quasi-reversible or reversible when the temperature is higher than 873 K. Kuznetsov [33] revealed that as the melt basicity increases, number of electrode processing stage decreased and a transition from the reversible to irreversible process of electrochemical reaction occurred. However, although many efforts have been paid to the Ir electrodeposition, the electrochemical behavior of Ir^{3+} ions in melting NaCl-KCl-CsCl and corresponding electrochemical mechanism were rarely reported. It was unfavorable for the further improvement of Ir coating.

In this work, the electrochemistry and major kinetics parameters of Ir^{3+} ions in the NaCl-KCl-CsCl melts were studied. The influences of deposition parameters on the microstructure of Ir coatings and the corresponding electrochemical mechanism were also discussed, which may provide more insights for better understanding of electrodeposition of Ir coatings from the melting chlorides.

2. Experimental

2.1. Chemicals

All operations of chemicals were carried out under the inert argon atmosphere. After being dried under vacuum at 423 K for 24 h, equal mole anhydrous NaCl, KCl, CsCl (analytical grade, Alpha Chemical Reagent Co., Ltd) were mixed and used as the supporting electrolytes. The temperature deviation of melts, which was measured using a nickel-chromium thermocouple packed by a closed-end quartz tube, was maintained within ±2 K. After being completely melted, the melts were pre-electrolyzed for several hours to remove impurities. Ir^{3+} ions was introduced into the bath through anhydrous $IrCl_3$ powder (purity: 99.99%, Shanxi Kaida Chemical Engineering Co., Ltd).

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2.2. Electrochemical electrodes and apparatus

Ag/AgCl (1 wt%AgCl) and Ir^{3+}/Ir were used as the reference electrodes (RE) in different experiments. The former was made of the silver wire (Φ1.0 mm, 99.99%, China New Metal Materials Technology Co., Ltd), which was immersed into the melting NaCl-KCl-CsCl with 1.0 wt.% AgCl contained in a thin-walled quartz tube with an capillary pore. The latter was made of the pure metallic Ir strip (2.0 × 2.5 × 100 mm, 99.95%, China New Metal Materials Technology Co., Ltd), which was immersed directly into the solution of NaCl-KCl-CsCl molten salts containing $IrCl_3$. Platinum wires (Φ1.0 mm, 99.99%, China New Metal Materials Technology Co., Ltd) and Ir strips sealed in corundum tube with Pyrex glass, which had been polished by abrasive papers, ultrasonically cleaned in deionized water and dried in vacuum at 423 K successively, were used as the working electrodes (WEs). Counter electrodes were made up of graphite rods (Φ10 × 100 mm SGL Carbon Co, Ltd.), which were polished and cleaned in acetone prior to each experiment.

2.3. Electrochemical measurements

All electrochemical measurements were performed using a CHI660E potentiostat-galvanostat electrochemical workstation controlled by a computer with the CHI version 14.01 software package. Transient and steady electrochemical techniques, i.e. cyclic voltammetry (CV), liner sweep voltammetry (LSV), chronopotentiometry (CP) and electrochemical impedance spectrum (EIS) were measured to explore the electrochemical reduction of Ir^{3+} ions in the melts. In order to confirm reproducibility of the experiments, electrode cleaning process was performed and electrochemical operation was stopped for 20 min to reach the temperature and composition equilibrium of the melts.

2.4. Electrodeposition of Ir coatings on Re coated graphite substrate

Graphite rods (Φ10 × 50 mm, SGL Carbon Co, Ltd.) whose surface was polished by abrasive papers and ultrasonically cleaned in acetone for 15 min, were used as substrates. Re layers were prepared on the graphite substrates as the transition layers between the substrates and Ir coatings.

Re layers on graphite substrates were prepared by chemical vapor deposition (CVD) with the device reported in previous work [21,22]. Graphite substrates were treated at 1573 K for 10 min under argon atmosphere, to remove entrapped gases and impurity. Rhenium layers with the thickness of 20–25 μm were prepared by the thermal decomposition of $ReCl_5$, with the chlorination temperature of 973–1173 K, deposition temperature of 1273–1573 K, flow rate of chlorine (purity: 99.999%) of 50–100 mL/min, flow rate of argon (purity: 99.999%) of 100–500 mL/min.

Ir coatings on Re coated graphite substrates (Φ10mm × 60 mm) were prepared by electrodeposition, which were carried out in the equal mole NaCl-KCl-CsCl ternary electrolyte containing 0.20 mol/L $IrCl_3$. The cylinder graphite crucible (Φ90 mm × 130 mm) which was degassed at 1773 K for 1 h in a vacuum furnace before used and stored the electrolyte salts was used as the anode. While the disk cathode was made up of the Re coated graphite rods inserting in the quartz tubes with 10 μm inside diameter. Pure Ir strips immersed into the melts used as REs. The parameters of Ir electrodeposition was listed in Table 1.

The morphology of Ir coating was observed by scanning electron microscope (SEM, Hitachi S-4800). The energy dispersion spectroscopy (EDS) was performed by GSM-6360LV to determine the composition of coating.

Table 1
electrodeposition parameters of Ir coating on Re coated graphite.

Groups	Current or potential	Temperature (K)	Others
1	−20 mA/cm^2	823	electrolyte: NaCl-KCl-CsCl
2		853	
3		883	C_{Ir3+}: 0.20 mol/L
4		913	
5	−0.03 V	853	substrate: Re coated graphite (1.13 cm^2)
6	−0.10 V		
7	−0.15 V		
8	−0.20 V		

3. Results and discussions

3.1. Electrochemical reduction of $IrCl_3$

Fig. 1 shows a family of CVs with the scan rate ranging from 0.05 V/s to 0.40 V/s obtained on the Pt electrode at 883 K in the NaCl-KCl-CsCl melts containing 0.2 mol/L $IrCl_3$. A couple of redox current peaks corresponding to the electrochemical deposition/dissolution of Ir are appeared at about −0.20 V and +0.30 V when the scan rate is 0.05 V/s. While the peaks of cathodic and anodic current are dumpy. There is another anodic peak when the potential increases to about +0.40 V which should correspond to the anodic reaction of Cl^- ions in the melts, because only the Cl^- ions in the melts can lost its electrons to form anodic current peak in the CVs.

The CVs at different scan rates were considered as the solution regarding to reversibility of the electrochemical reaction though application of peak-voltammetry theories. As shown in Fig. 1, as the scan rates increases from 0.05 V/s to 0.40 V/s, the cathodic peaks shifts negatively and the anodic peaks shifts positively accordingly. According to peak-voltammetry theories [34], the cathodic peak potential E_p is a function of the scan rate v for the quasi-reversible or irreversible reaction, while it is independent of the scan rate v for the reversible reaction. That is to say, electrochemical reduction of Ir^{3+} ions should be a quasi-reversible or irreversible reaction.

The relationships between cathodic peak current i_p, cathodic peak potential E_{pc} and scan rate v are displayed in Fig. 2a and b, respectively. As can be seen, i_p linearly increases with square root of the scan rate $v^{1/2}$, while E_{pc} is linearly dependent of $\ln v^{1/2}$. According to Matsud and Hubbard [35,36] [37], the electrochemical reduction of Ir^{3+} ions is an diffusion-controlled irreversible reaction, for which the peak potential E_{pc} and $\ln v^{1/2}$ has a relationship as [38]:

$$E_{pc} = b - \frac{RT}{\alpha F} \ln v^{1/2} \quad (1)$$

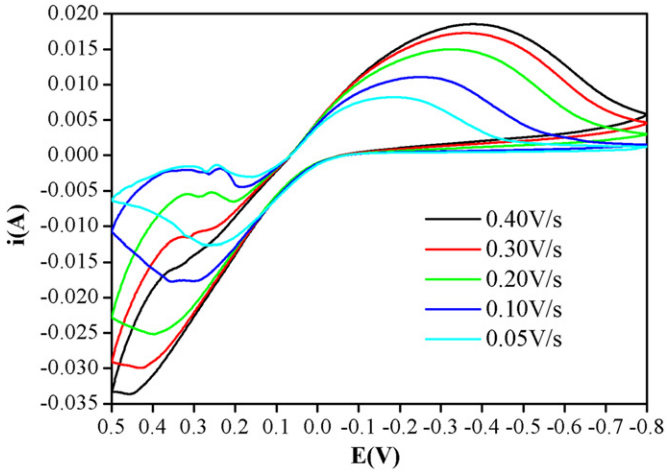

Fig. 1. A family of CVs on the Pt cathode at 883 K in NaCl-KCl-CsCl molten salts containing 0.2 mol/L $IrCl_3$: −0.90 V (vs Ir/Ir^{3+}) ~ +0.50 V (vs Ir/Ir^{3+}), scanning rate 0.05 V/s–0.40 V/s.