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Electrochemical dissolution of metals of the platinum group by alternating current

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The electrochemical dissolution of metals of the platinum group in acid solutions using an alternating current is investigated. It is shown that this is an efficient and promising method for the production of pure noble metal salts, and for the analysis and extraction of small amounts of noble metals from waste and poor ores. The production of pure bromides and chlorides of gold and rhodium is particularly efficient because their rates of dissolution are high. The mechanism of the influence of the alternating current on the metal/electrolyte interface is also discussed.

1. Introduction

Compounds of noble metals are widely used in various fields in engineering and technology [1]. The metals of the platinum group are not soluble in acids and ruthenium, rhodium and iridium cannot be dissolved even in aqua regia. Although platinum, palladium, osmium and gold are soluble in aqua regia, the use of this solvent on an industrial scale is undesirable. The production of pure noble metal compounds is associated with various technological problems. For example, rhodium is either sintered with barium peroxide and the product dissolved in hydrochloric acid, or chlorinated in the presence of sodium chloride at high temperatures, or dissolved in a mixture of nitric and hydrochloric acids at 300 °C under 240–270 atm pressure [2]. Rhodium bromide is obtained by the prolonged heating of the metal in the presence of hydrobromic acid and bromine [3]. Gold compounds are produced by chlorination at high temperatures [4].

The electrolytic dissolution of metal powders involves the additional difficulties of providing conduction. Anodic dissolution is widely used for the dissolution of ruthenium [5], of silver [6–9], gold [10–13], iridium [14] and other noble metals in various solvents and melts. However, the anodic dissolution of noble metals in acids is difficult, due to the passivation of the metals [15–17].

Despite the low dissolution rates [15] electrochemical techniques are more efficient for large scale commercial production [18] than cumbersome and laborious high-temperature sintering [2], chlorination [3, 19] and melting [20].

It is generally accepted that the activating effect of alternating current on inert noble metals is explained by the parallel processes of metal dissolution and the formation of passivating oxide films on the surface, which prevents dissolution during the anodic half-period of polarization. In the cathodic half-period the oxide film reduces and the ability of the metal to dissolve is restored.

However, there may be an electromechanical action of the alternating current at the electrolyte/electrode interface which contributes to dissolution.

This paper is concerned with the investigation of the electrolytic dissolution of noble metals and their powders in acids and aims to broaden understanding of the dissolution mechanism at the electrode/electrolyte interface under the influence of alternating current.

2. Experimental details

Electrodes, made of wires 0.5 mm in diameter and plates 5 mm wide and 0.3 mm thick, were dipped into the electrolyte to a preset depth using a micrometer. The moment at which the electrode made contact with the solution was registered by an ohmmeter. The rate of dissolution was determined either by the loss of weight of the wire electrode or by measuring the concentration of the dissolution product.

A schematic diagram of the electrolyser for the dissolution of powder-like noble metals is shown in Fig. 1. This consists of a glass or quartz two-cell system (1) connected by an electrolytic bridge. The cells were conical to allow the powdered metal (2) to be placed into them. Spectrally pure current-conducting graphite electrodes (3), jacketed in either glass or quartz, were introduced into the cell through ground glass connections. The glass/quartz jacket (4) was sealed in order to prevent the electrolyte penetrating it. The sharpened ends of the electrodes were

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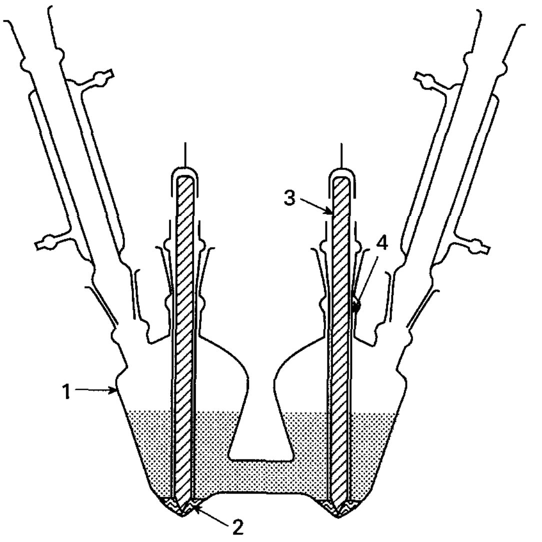

Fig. 1. The electrolyser for dissolution of powder-like noble metals. Key: (1) quartz tow-cell system, (2) metal powder, (3) graphite electrodes and (4) sealed jackets.

immersed in the noble metal powder. The cells were filled with the solution of prepared composition and a 50 Hz alternating current controlled by an autotransformer was passed through it. The electrolyser was equipped with reflux condensers to prevent the electrolyte from evaporating at high temperatures.

Figure 2 shows a schematic diagram of a glass U-shape electrolyser designed to dissolve substantial amounts of metal powders. The powder to be dissolved was placed at the bottom of the vessel. Graphite electrodes were used throughout. Such electrolysers, if connected in series or in parallel, can form a battery for any preset productive capacity. The dissolution procedure must be performed at a high current density (up to 5 A cm^{-2}).

The temperature in both electrolysers was controlled with an accuracy of ±0.2 °C by means of a thermostatted bath.

Concentrated hydrochloric and hydrobromic acids (analytical grade) were used throughout. Prior to each experiment the surfaces of the electrodes were degreased.

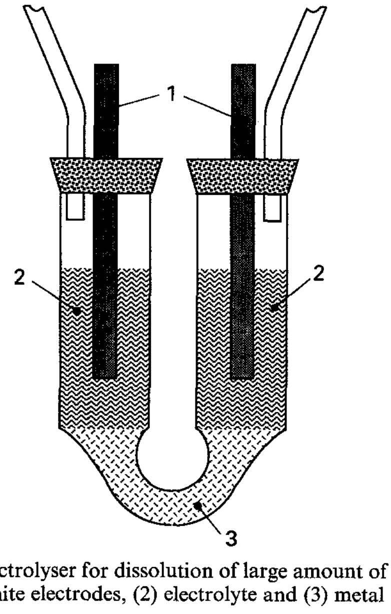

Fig. 2. The electrolyser for dissolution of large amount of powders. Key: (1) graphite electrodes, (2) electrolyte and (3) metal powder.

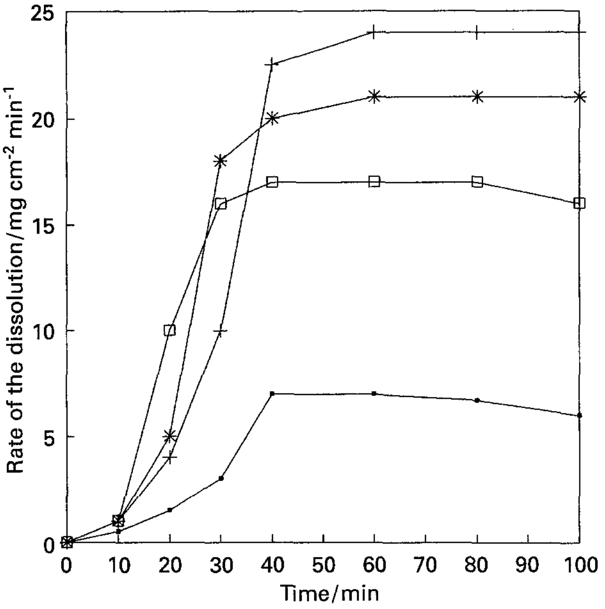

Fig. 3. The dependence of the dissolution rate of the platinum group metals on time (i – 3.5 A cm^{-2}, [HCl] = 11.6 N, t = 45 °C). Key: (■) iridium; (+) rhodium; (∗) platinum and (□) palladium.

3. Experimental results

The dissolution of ruthenium in hydrochloric acid with an alternating current resulted in a red–brown Ru(3+) compound which was likely to be the complex $H_2[RuCl_5 \cdot H_2O]$. After evaporation in a flow of dry HCl, a complex ($RuCl_3 \cdot H_2O$), soluble in water or alcohols was formed. Rhodium dissolved in the form of the crimson-red coloured Rh(3+) halide. The compound was stable and evaporation was performed without HCl or HBr flows. As a result, $RhCl_3 \cdot 3H_2O$ and $RhBr_3 \cdot 0.5H_2O$ complexes were formed. Palladium dissolution lead to a $H_2[PdCl_4]$ complex. The valence of iridium and platinum in the solution was found to be four. The orange–red coloration of $H_2[IrCl_6]$ solutions resembled the colour of ruthenium compounds. The dissolution of gold resulted in a gold-hydrochloric acid $H[AuCl_4]$ complex of a yellow colour.

The kinetic curves of the dissolution of noble metals are presented in Figs 3–7. As illustrated in Fig. 3, the dissolution of platinum metals in hydrochloric acid was characterized by the presence of an induction period due to the removal of a passivating oxide film. The rate of the dissolution increased with temperature (Fig. 4) and with current density (Fig. 5). The induction period depended on the current density (Fig. 6) and was affected by pretreatment.

For example, the reduction of the oxide film during the cathodic prepolarization substantially shortened the induction period (curve 1, Fig. 6). Similar results were obtained if an iridium powder was reduced in a hydrogen furnace.

In the case of powdered rhodium, dissolution in either acid had a short induction period. The dissolution

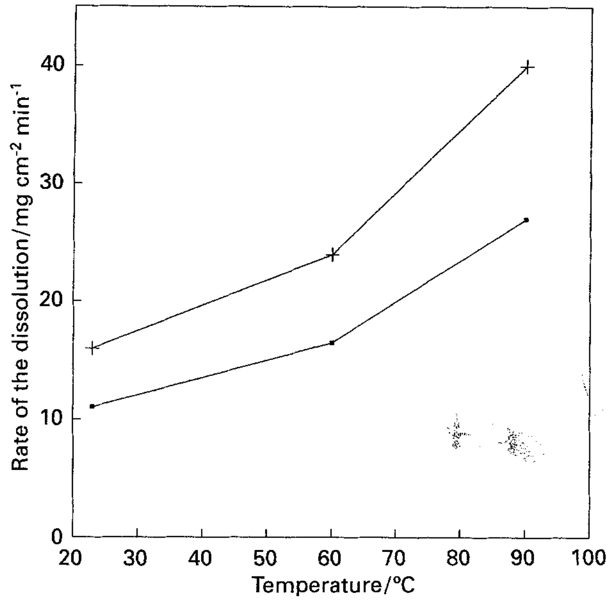

Fig. 4. The dependence of metal dissolution rate on electrolyte temperature ($i = 5\,\mathrm{A\,cm^{-2}}$, [HCl] = 11.6 N). Key: (■) palladium and (+) rhodium.

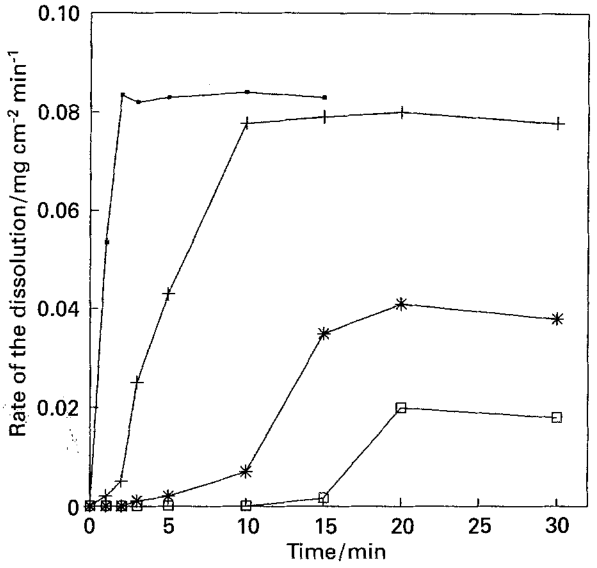

Fig. 6. The dependence of an induction period of the iridium dissolution on the current density, i: (■) cathodic pretreatment at $5\,\mathrm{A\,cm^{-2}}$ for 3 h, then $i = 3.5\,\mathrm{A\,cm^{-2}}$; without pretreatment, i: (+) 3.5; (*) 3.0 and (□) $2.0\,\mathrm{A\,cm^{-2}}$.

rate reached an almost steady value (similar to a 'limiting current') with increase in current density (Fig. 5). At the maximum current, sparking and vigorous gassing deteriorated the contact between the powder and the tip of the electrode. The dissolution regime became unstable and uncontrollable thus making further increase of the current density impossible. Free bromine condensed in the cooler when rhodium was dissolved in hydrobromic acid.

In the case of gold dissolution in hydrochloric acid (Fig. 5) the 'limiting current' was clearer. The dependence of the dissolution rate on the current density showed hysteresis. When a gold electrode was polarized by an alternating current of small amplitude, its surface was covered with an orange passive film while the dissolution rate was low. The films were smooth and homogeneous at low i values, and developed microroughnesses as the current density increased.

The film disappeared when the current density was $20\,\mathrm{A\,cm^{-2}}$ and vigorous dissolution began, also accompanied by sparking and overheating. However, gold activity remained the same even if the current density was lowered to $5\,\mathrm{A\,cm^{-2}}$. During the process of active dissolution (the rate of dissolution was larger than $4\,\mathrm{g\,cm^{-2}\,h^{-1}}$) the gold surface was mirror like. When the gold was activated by a high current density of $20\,\mathrm{A\,cm^{-2}}$, the metal remained active and the dissolution proceeded smoothly. During active dissolution, gold dissolved 30 times faster than in aqua regia. Thus, this

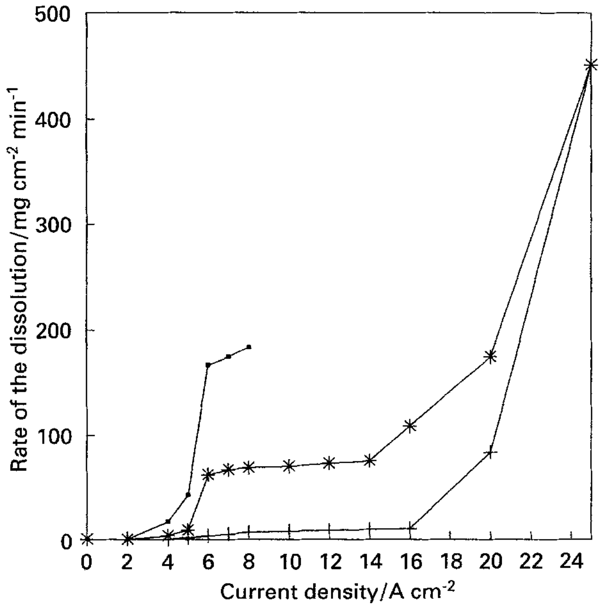

Fig. 5. The dependence of the dissolution rate on alternating current density ([HCl] = 11.6 N, $t = 65\,°\mathrm{C}$). Key: (■) rhodium; (+) gold on increase of current density and (*) gold on decrease of current density.

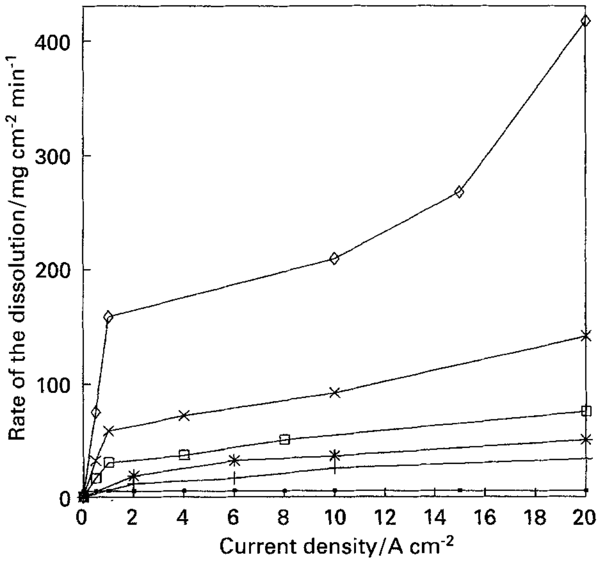

Fig. 7. The dependence of the dissolution rate of magnetite in HCl on the value and type of current: (◇) alternating current, (×) half-wave rectified anodic current, (□) half-period rectified cathodic current, (*) anodic direct current, (+) cathodic direct current and (■) chemical self-dissolution without current.

method of dissolution is a promising technique especially when large amounts of gold halides are required. In particular, such a technique has the advantage of producing nitrate-free halides. At $i < 5\,\mathrm{A\,cm^{-2}}$ the dissolution rate decreased sharply and the electrode became passive again.

Passivation was due to the formation of an oxide film. Neither chlorides nor bromides were detected analytically in the film. Gold, which had its surface freed from oxides during the cathodic reduction, dissolved anodically with 100% current efficiency. Above a potential of +1.1 V vs SCE the current efficiency fell because of the formation of a stable passive film [15]. It is likely that under the action of an alternating current of small amplitude, the formation of such a film takes place faster than its reduction. However, the dissolution did not stop completely and the state of the passive film changed with time.

The rate of iridium dissolution was significantly lower than that of rhodium. This probably happened due to the capability of iridium ions to reduce to the +3 valence during cathodic half-periods and oxidize to the +4 valence state during anodic half-periods. In general, compounds of an intermediate valence are characteristic of many noble metals. They could be accumulated in solution, reaching appreciable concentrations. The formation of mirror-like surfaces on the electrolyser walls was likely to result from the disproportionation of these compounds during abrupt cooling.

We have measured the rates of metal dissolution using direct and half-wave rectified current (see Table 1). In all cases the rate of anodic dissolution by half-wave current was higher than that of the dissolution by smoothed anodic current, while the dissolution rate under an alternating current treatment was several orders of magnitude higher than both direct and half-wave current rates. This is natural if the small thickness and high electric conductivity of passive films of transition metals are taken into account. Complete removal of the passive layer during cathodic polarization also led to more efficient electrode activation.

The total effect of alternating current is not only due to chemical action but also involves electromechanical effects. The oxide film is a dielectric with piezoelectric properties. The mechanical stresses resulting from the application of alternating current disturb the integrity of the film, thus causing the surface to be depassivated. Reorientation of the electrolyte dipoles in the vicinity of the electrodes also contributes to the disintegration of the passive film.

Natural magnetite (Fe_3O_4) was used as a model to check the role of the piezo effect in the surface depassivation process. Fe_3O_4 possesses piezoelectric properties and has sufficient conductivity to enable it to be used as an electrode in hydrochloric acid. However, magnetite, like any other model, has a drawback, namely that iron ions are capable of changing their valence from 2 to 3 (and vice versa) under the action of anodic and cathodic half-periods. The dissolution rates of magnetite were measured under the action of alternating, half-wave rectified, and direct current of both signs (Fig. 7). An alternating current dissolution rate was slightly higher than twice the dissolution rate using half-rectified anodic current dissolution (Table 1). This confirms the presence of the electro-mechanical effect of an alternating current. Indeed, if the piezo effect were the only contributor to the disintegration of the passive film the alternating current dissolution rate would be twice as large as the rate using the half-rectified current.

Table 1. Normalized rates of metal dissolution under the action of direct and half-wave rectified current

Material	*Normalized rates of dissolution**				*Current density* /A $\mathrm{cm^{-2}}$
	Alternating current	*Half-wave rectified current*		*anodic direct current*	
		anodic	*cathodic*		
Ir	4×10^6	350	1	6.5	3.5
Pt	7.3×10^6	400	1	6	3.5
Au	3.8×10^7	700	1	13	7
Fe_3O_4	5.1	2.0	1	0.6	3.5

* All normalization was with respect to the half-rectified cathodic current value.

4. Conclusion

The alternating current dissolution of noble metals is a convenient and promising method for the production of pure rhodium, ruthenium, palladium, iridium, platinum and gold chlorides. We have used the method in our laboratory to extract rhodium, iridium, platinum, palladium and ruthenium from wastes and to prepare standard solutions of these metals for analytical purposes, as well as for the extraction of gold from poor ores.

Experiments on magnetite support the notion that electromechanical effects may contribute to the breakdown of the passivating film.

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