

Electrochemical interactions of industrially important platinum-containing minerals

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Abstract

Pt–Te₂ and Pt–Bi–Te are two important platinum-carrying minerals typically found in altered platinum reserves. Mineralogical studies indicate the Pt–Pd–Bi–Te class to react poorly on the flotation stimuli and indications are that these minerals are slow floaters. This paper investigates the fundamental interactions of potassium ethyl xanthate with these minerals by employing electrochemically controlled contact angle measurements, FT-IR spectroscopy and voltammetry. The electrochemical investigations revealed that Pt–Te₂ is more noble than Pt–Bi–Te at potentials lower than 300 mV (SHE) in sodium tetraborate buffer solution and the reduction peak observed during the return sweep of Pt–Bi–Te is mainly associated with the reduction of bismuth oxidation products. Both the minerals show increased anodic currents when polarised at 0.3 V (SHE) in a 0.05 M Na₂B₄O₇ solution containing 1×10^{-3} M potassium ethyl xanthate. According to the results of the rest potential measurements, formation of dixanthogen should be thermodynamically favourable and the very high rest potentials are attributed to the catalytic effect of platinum on the oxygen reduction reaction. The formation of dixanthogen on both the minerals was confirmed by *ex situ* FT-IR spectroscopy. Contact angle measurements revealed the surface of Pt–Bi–Te to be hydrophobic in nature whereas small contact angles were realized on Pt–Te₂. Surface roughness of the mineral could be responsible for these small contact angles.

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1. Introduction

In contrast to traditional platinum processing routes, recent advances in beneficiation technologies are also directed towards the recovery of platinum-group elements (PGEs) from altered deposits. Such altered deposits include the Platreef, the Great Dyke reserve in Zimbabwe and oxidised UG-2 and Merensky reefs. Open cast mining methods are employed in most instances because of the shallow nature of these reefs. The economic advantages of employing this mining method are counteracted by difficulties encountered during processing, resulting in lower PGE recoveries

than for unaltered Merensky and UG-2 ores. These platinum sources are usually characterised by the following: oxidised sulfides, altered gangue minerals (for example, serpentine in case of Platreef), a large portion of PGMs belonging to the classes Pd–Pt–Bi–Te (Great Dyke and Platreef ores), Pt–Pd–S–As, and PGE-alloy (for example PtFe in oxidised UG-2), poorer association with base metal sulfides, a large portion of PGMs associated with gangue minerals (regrinding is required to prevent excessive losses to the tailings), a large portion of PGMs liberated during milling and significant losses of liberated PGMs to tailings.

The occurrence of liberated PGMs in the tailings streams of the concentrators necessitates research on the oxidation and collector interaction of these minerals. There are practical indications that the recovery of the Pd–Pt–Bi–Te class from these reserves (Platreef and Great Dyke) is poor.

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Vermaak et al. (2004, 2005) performed an investigation on synthetic Pd–Bi–Te employing voltammetry, impedance measurements, Raman spectroscopy and microflotation. These studies indicated a very strong interaction of ethyl xanthate with Pd–Bi–Te resulting in the formation of a hydrophobic surface state. Dixanthogen and a metal xanthate species were identified on the surface by performing *in situ* Raman spectroscopy. The small size of the liberated PGMs, less than 10 μm , and interactions with the sulphide particles could contribute to the poor flotation response of these particles.

Similar to that of Pd, the Pd–Pt–Bi–Te class is a major Pt carrier and recent sharp increases in the platinum price have resulted in increased efforts to understand the flotation behaviour of this class. With more and more attention being given on the recovery of PGEs from altered platinum reserves, this work investigates the fundamental interactions of the most important platinum-carrying minerals typically found in altered PGE ores (i.e. Pt–Bi–Te and Pt–Te₂).

2. Experimental

2.1. PGM synthesis

The synthesis procedure of the synthetic crystals (Pt–Bi–Te and Pt–Te₂) is similar to that of Pd–Bi–Te, which is given elsewhere (Vermaak et al., 2004, 2005). Instead of applying a heat treatment lasting several days at 480 °C as used by Vermaak et al. (2005), a fully homogeneous microstructure was only obtained in this study by employing the heat treatment at 480 °C for up to 60 days.

A back-scattered electron imaging and XRD analysis performed on the synthetic crystals, provided no evidence of phases other than the intended Pt–Bi–Te, and Pt–Te₂.

2.2. Electrochemical investigations

A conventional electrochemical cell with a three-electrode system, consisting of a working electrode (synthetic mineral), platinum counter electrode and reference electrode, was used. The PGM crystals were mounted in resin and electrical contact was achieved between the contactor shaft and the mineral by employing a spring. Potentials were measured against a KCl-saturated Ag/AgCl reference electrode, which has a potential of +0.20 V on the standard hydrogen electrode scale. For all the electrochemical measurements, a potentiostat (Model PCI4/750) and electrochemical software (PHE200 Physical Electrochemistry Software) from Gamry Instrument Inc. were employed. Sodium tetraborate at a concentration of 0.05 M Na₂B₄O₇ was used to buffer the solution at pH 9.3. Electrolytes were prepared using analytical grade reagents and distilled water with a final resistivity of 18 M Ω ·cm. Prior to each experiment, the solution was de-aerated for 2 h with argon gas

(99.999%). When the electrochemical measurement commenced, the gas disperser was raised above the solution level to keep a slight positive pressure within the cell. Cyclic voltammograms were recorded at a scan rate of 1 and 20 mV/s starting from the most negative potentials going positively to the upper potential and then reversed. Polarisation diagrams were recorded at a scan rate of 1 mV/s. Electrochemical measurements were conducted after the open-circuit potential had stabilised. The solution was replaced between experimental runs to avoid contamination. Purified collectors were used in all the experiments. The surface of the PGM electrode was renewed between every experimental run by grinding with P-4000 grade silicon carbide under a constant stream of de-oxygenated distilled water.

2.3. Contact angle measurements

The electrodes were sequentially dry ground with 600 and 4000 grit silicon carbide paper prior to each experiment. The influence of dry and wet polishing for Pt–Bi–Te electrode was examined. The above-mentioned polishing treatment gave reproducible results. Supporting electrolytes of 0.05 M sodium tetraborate was used which provided a buffered solution of pH 9.3.

Regular de-ionized water (DI) was used in all of the experimental work. Ultra pure de-ionized water (UPDI) (18 M Ω ·cm) was used to study the difference between regular DI and UPDI water for the contact angle measurements. All other chemicals used were of analytical reagent grade quality. Prior to each experiment, the solution was de-aerated for 2 h with ultra high purity nitrogen. A conventional three-electrode system was employed with an EG&G Princeton Applied Research Potentiostat/Galvanostat (Model 173) to control electrode potential. The contact angle measurement (captive bubble with mineral electrode facing down) procedure involved stepping the potential to the required value for 5 min. The contact angle was measured directly after polarisation was terminated (open-circuit conditions). A nitrogen bubble was introduced to the surface and contact angles were measured on both sides of the bubble. A number of bubbles were placed as quickly as possible on the surface from which contact angles were measured. A standard deviation and 95% confidence interval were determined of the contact angles measured for the different runs. Latex gloves were worn throughout the experiments to avoid the contamination of the mineral surfaces.

2.4. FT-IR spectroscopy

Complementing electrochemical investigations with studies using FT-IR reflection spectroscopy have provided valuable information on the nature of the surface species. The FT-IR spectra of surfaces of the electrodes were recorded with a Perkin–Elmer GX 2000 FT-IR Spectrometer, adapted with Perkin–Elmer Auto Image Microscope

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