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PROCEEDINGS

XXIV International Conference
Ecological Truth

Editors
Radoje V. Pantovic
Zoran S. Marković

EcoIst '16

12 – 15 June 2016
Hotel "BREZA" Vrnjacka Banja,
SERBIA

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RECYCLING OF PLATINUM FROM CRUCIBLES FOR MELTING AND CASTING

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ABSTRACT

The aim of this study was the recycling of platinum from crucibles for melting and casting. This paper has considered the possibility of direct melting of crucibles as well as the possibility of processing the crucibles by PMS methods (shaking table and flotation concentration). Laboratory studies have shown that leaching of ground crucibles in sulfuric acid has achieved the leaching degree of magnesium oxide of 99.98% thus providing a material suitable for melting.

Key words: platinum, recycling, flotation, leaching.

INTRODUCTION

Platinum group metals (PGMs) play a key role in the modern society, as they specific importance for clean technologies and other high-tech equipment. Important applications beyond the well-known areas of chemical process catalysis and automotive emissions control include information technology [1-2]. Precious metals, especially platinum, are important catalytic materials for many chemical reactions. For example, platinum is used in some fuel cells; however, a broad commercialization of such fuel-cell technology is hampered by the fact that platinum is rare and thus far too expensive [3].

Development of modern industry is inconceivable without the use of products of platinum and platinum-based alloys. The use of platinum dating from the ancient times, and platinum in Europe was brought by Vood in 1735, and Brownrig Vatsoh were the first who described its characteristics. Platina del Pinto from Čoka (Colombia) attracted the attention of Antonio de Utloae in 1748, and Slalieer from Leiden even more in 1558 mentioned some non-melting metal, which was considered to be platinum [1]. Due to its color, unique physical-chemical properties, the demand for platinum is growing in the chemical industry, automotive industry, medicine, jewelry production, etc. [2, 4]. Also, platinum is irreplaceable material in making corrosion-resistant and fire-resistant chemical apparatus and vessels of various purposes.

Such a wide range of application the platinum and platinum based alloy leads to increased demand in the world for this metal. One way to ensure the adequate amounts of platinum is to increase the exploitation of ore deposits [5]. This however, does not lead to the sustainable development, and the efforts are directed towards increasing the degree of recycling the secondary raw materials (waste electrical and electronic parts, jewelry, consumable dental and orthopedic materials, used catalysts, etc. [6-9].)

Recycling platinum is a difficult, complicated process. The first step is the dissolution of the used platinum in highly corrosive aqua regia, a mixture of nitric and hydrochloric acids, or a highly oxidizing mixture of sulfuric acid and hydrogen peroxide, known as piranha [3].

In the Mining and Metallurgy Institute Bor, the Profit Center Processing of platinum metals as the secondary raw materials, the ceramic melting crucibles of melting (MgO) and casting nozzles (Al_2O_3) appear from own production. These crucibles contain in their composition Pt, MgO and Al_2O_3. The aim of research was to develop the technology for processing the crucibles that are used for melting and casting of platinum in order to obtain the platinum purity of 99.99.

EXPERIMENTAL PART

Chemicals

Amylopectin (starch), collectors of potassium amyl-xanthate (Župa Kruševac), Aero 3302 promoter (Cytec) and frothers Dowfroth 250 (Dow) and Aerofroth 65 (Cytec) were used in laboratory research. Sulfuric and nitric acid p.a. quality (Zorka Šabac) were used for leaching of crucibles.

Methods and Apparatus

To determine the chemical composition of electrolyte and control the concentration of Pt, Mg, Al and impurities was used (ICP-AAS Manufacturer: Spectro, Model: Ciris Visio, detection limit < 0.0001 g/dm^3).

To record the X-ray diffractogram was used the model: EXPLORER, manufacturer: GNR Analytical Instruments Group, Novara, Italy.

Physico-chemical characterization of material

In order to determine the optimal way of processing in experimental work, a detailed physico-chemical characterization of crucibles was carried out.

The chemical analysis results obtained by the instrumental analytical chemistry are shown in Table 1, and the X-ray diffractogram is shown in Figure 1.

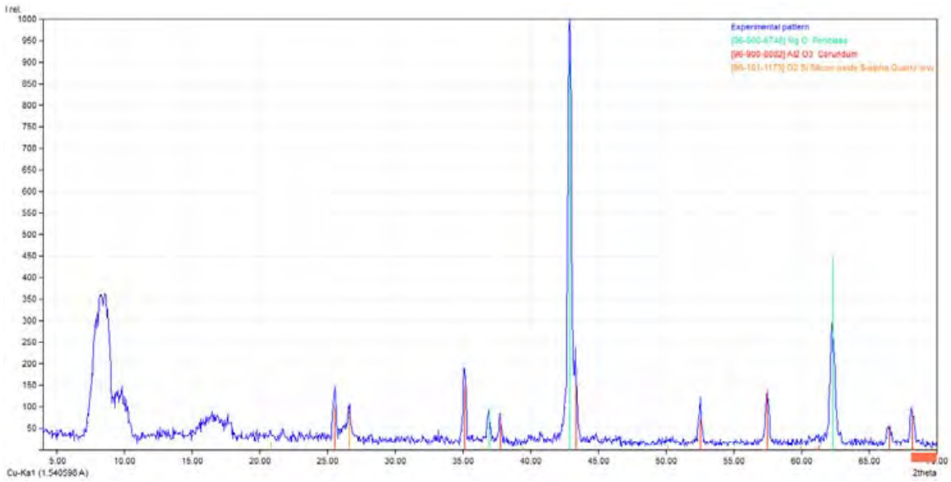

Figure 1. X-ray diffractogram of ground crucibles

X-ray diffractogram (Figure 1) shows two intesive peaks corresponding to periclase (MgO) and corundum (Al_2O_3). Besides these two minerals, the presence of quartz can be seen on diffratogram. Since that this method can not detect the low levels of impurities, the samples were analyzed by AAS method (Al_2O_3, MgO, Ca i Fe), G (SiO_2) and ICP AAS (Pt).

Table 1. Chemical composition of milled crucibles

	SiO_2 G	Al_2O_3 AAS	MgO AAS	Ca AAS	Fe AAS	Pt ICP-AES
%	8.28	36.55	45.36	1.52	0.99	0.28

It can be seen from Table 1 that the main component in a sample are MgO and Al_2O_3.

RESULTS AND DISSCUSION

Theoretical Considerations of Direct Melting of Crucibles

Milled crucibles and casting nozzles, (chemical composition shown in Table 1), are very difficult to process using the pyrometallurgical processes.
The melting temperature of this mixture (45.36 %MgO, 36.55 % Al_2O_3 and 8.28 % SiO_2) is about 2300°C (Figure 2).

The main reason for this is the impossibility of forming the mixtures with a low melting of slag, which would provide a flowable slag and good layering with the metal collector (which allow minimum losses of collector and precious metals with slag) and simultaneous heating of collector metal to the casting temperature without oxidation. Components of material for processing have extremely high melting temperature MgO-2800 °C, Al_2O_3-2020°C, SiO_2-1723 °C as well as the flux and addition in pellets at CaO-2570 °C [10]. The phase diagram of the system MgO-Al_2O_3-SiO_2 is shown in Figure 2.

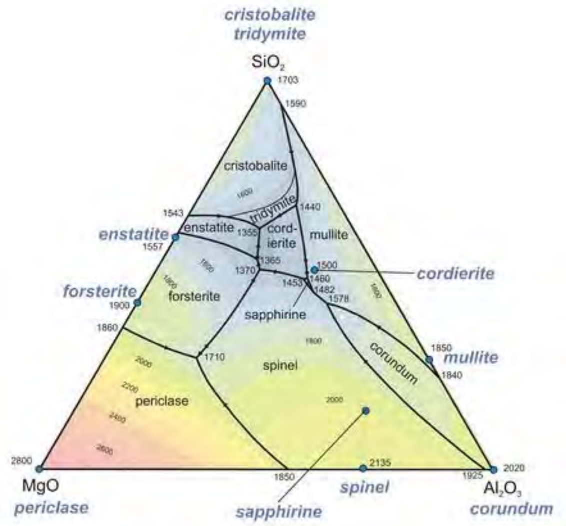

Figure 2. Phase diagram for the system $MgO\text{-}Al_2O_3\text{-}SiO_2$ [10]

Melting temperature of material slag is mainly over 1600 °C, with very narrow intervals where the temperature is slightly lower and that are highly sensitive to the slightest change in chemical composition. With change of some batch component from 1 to 1.5%, the melting temperature may rise for 250-300 °C, what leads to "freeing" the bath surface. On the other side, the brick of furnace (Birlac furnace) can withstand the bath temperature of max. 1550 ^oC. Also, the collector metal will at such high temperatures "burn out" (oxidized) and as such cannot be processed by electrolytic refining. In addition, to achieve high temperatures in the furnace, the electricity consumption is significantly higher.

Due to this reason, it is necessary, before to melting, to process the material by hydrometallurgical method in the aim to reduce MgO content below 5% and in this way to ensure the batch with eutecticum in the temperature range of 1330 to 1350 °C. In doing so, the care must be taken that variation in chemical composition of batch of a few percentages can lead to occurrence of peritectum points with high melting temperature above 1567 °C. So, in terms of pyrometallurgy, it is necessary that MgO content in mixture is below 5%.

Possibility of Preparation the crucibles for Melting by the Mineral Processing Methods

Sample of used crucibles for platinum melting was homogenized. From sample, the excluded smaller samples were tested on a shaking table and by the method of flotation concentration to obtain material that would be suitable for further metallurgical treatment. The aim of this testing was to concentrate platinum or to reduce MgO below 5% from the product with platinum.

Testing the Possibility of Concentration on a Shaking Table

Sample for concentration experiment on a shaking table, in the amount of 1 kg was crushed by impact crusher to the grain size - 1.40 mm. Four products according to the density of particles were separated in a thin layer of water current. Visually, there was no the satisfactory separation. It was expected for platinum to go in the heaviest product of a shaking table, the so-called concentrate. Since this is a sample that is not only polymineral but is composed of mineral grains of a wide range of sizes, the heaviest grains, i.e. coarse, large and small, went to the heaviest product. Due to this reason, the heavy product was sieved into three size classes and then each one was observed under a microscope.

Based on a visual assessment concentration process and microscopic observations of the heaviest faction, it was concluded that the shaking table cannot provide samples with less than 5% MgO.

Testing the Possibility of Flotation Concentration

Samples of 500 g were excluded from the starting sample. One of these samples was ground by the wet process in a ball mill in the presence of collector. Figure 3 shows the scheme according to which the experiment of flotation concentration was carried out. Amylopectin (starch) was added in order to deprivation MgO, and due to very bad foam with frother Dowfroth 250, the frother Aerofroth 65 was added until the appearance of foam. From collectors, the Aero 33023 promoter was used that was added at the stage of grinding and the KAX that was added in the conditioning phase. Balances of platinum and MgO are shown in Table 2.

Table 2. Balance of platinum concentration from sample "crucibles"

Product	m, %	Pt, %	Distribution Pt, %	MgO, %	Distribution MgO, %
Total	100.00	0.2857	100.00	56.67	100.00
Concentrate	1.57	1.9	10.43	40.14	1.11
Tailings	98.43	0.26	89.57	56.93	98.89

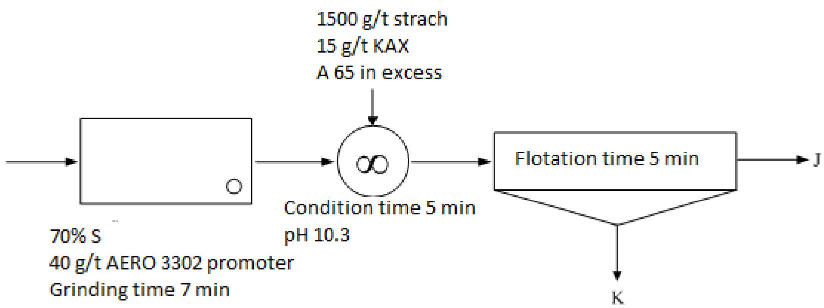

Figure 3. Technological scheme of flotation concentration the sample "crucibles"

Experiment of flotation concentration did not give the results because there was no satisfactory concentration of platinum as well as lowering the MgO content. Grinding time was chosen on the basis of experience while the reagent regime was selected from literature data relating to the natural mineral raw materials and not on artificially obtained materials [11,12].

Leaching

In order to reduce MgO content below 5%, the samples of crucibles were leached in sulfuric acid (the cheapest and most suitable for further melting) at different conditions. Leaching conditions were chosen on the basis of previous experiences and reviews of literature [2]. Leaching was carried out in two stages.

I stage: Testing of the effect of acid on leaching degree of magnesium oxide.

The samples were leached in sulfuric acid at 60 °C with the ratio of S:L = 1: 20 for a period of 6 h with stirring (400 min^{-1}):

I_1: leaching with 15% sulfuric acid

I_2: leaching with 20% sulfuric acid

I_3: leaching with 30% sulfuric acid

The first stage of research showed that the highest leaching was achieved by 20% sulfuric acid.

II stage: Two experiments were carried out in this stage of research:

II_1: leaching with 20% sulfuric acid without stirring and additional heating,

II_2: leaching with 20% sulfuric acid with stirring, heating and addition of nitric acid.

Table 3 shows the testing results for both stages.

Table 3. Leaching degree of magnesium (content of Mg was determined by AAS method)

	Leaching conditions	% leaching MgO
I_1	15% H_2SO_4; t=60°C	98.35
I_2	20% H_2SO_4; t=60°C	99.60
I_3	30% H_2SO_4; t=60°C	97.20
II_1	20% H_2SO_4; t=25°C	96.55
II_2	20% H_2SO_4; t=25°C +10%HNO_3	95.32

CONCLUSION

After a detailed physico-chemical characterization of sample, as well as the theoretical considerations of direct melting the crucibles for melting and casting of platinum, it can be concluded that this mixture cannot be directly melt due to the high tempererature of eutecticum. It is possible to melt this mixture only if MgO content is reduced to below 5%. Research the possibilities of processing the crucibles using the mineral processing methods (shaking table and method of flotation concentration) did not give the satisfactory results. Leaching in sulfuric acid has achieved MgO leaching from 95.32 to 98.35%, which provided MgO content of less than 5% and therefore the conditions for this mixture melting.

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